Final Report

on

STUDY OF MEMORY ELEMENTS
HAVING TWO RESISTANCE STATES

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ABSTRACT

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Bistable silver sulfide resistive memory elements are obtained by pressing the pure compound, together with silver and platinum electrodes, into thin pellets. The elements are formed by steady application of voltages in the range of 1 to 10 volts, the time required being less the higher the voltage. Thereafter, pulses of the proper polarity in the range of 2 to 12 volts and 15 milliseconds duration are sufficient for switching between the stable high and the stable low resistance states. The ratio of the resistances of the high state to the low state may be 3 to 100 or more, depending upon the switching voltage. The energies required to switch are of the order of magnitude of 10^{-4} to 1 watt-second, depending upon the applied voltage. Switching occurs during the application of the pulse. Stored information may be read nondestructively with 2 volts. For resistance ratios greater than 4, life-times as high as 3×10^{5} cycles were obtained in cycling tests; the failure-to-switch rate is about 5%. The elements operate in vacuum, at -196° C, and at elevated temperatures with reduced energies; stored information survives exposure to 125° C, or to electron bombardment. In dynamic switching the element shows a current-voltage hysteresis pattern which may be interpreted in terms of a self-heated thermistor. Comparisons of the characteristics of silver sulfide, antimony trisulfide and nickel oxide, as memory elements, show silver sulfide to be the preferable choice for space applications.

Further studies are desirable to obtain higher reliability through testing of other methods of fabrication, and to evaluate further the characteristics of the element with respect to operation in the space environment.

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A STUDY OF MEMORY ELEMENTS HAVING TWO RESISTANCE STATES

CHAPTER I. INTRODUCTION

BACKGROUND

Prior to the initiation of the work reported herein, the UNIVAC Research Division had studied the potential usefulness of electrochemical cells as devices for storage of digital information. These studies led to the development of a voltaic cell with a solid electrolyte consisting of a solid solution of two silver halides[1]. In addition to the halides examined in the course of this study, silver sulfide was tested for its suitability as a solid electrolyte. Attempts to charge a cell with this compound as the electrolyte were not successful because no stable potential difference was developed across the electrolyte; this is a consequence of the relatively high electronic conductivity of the silver sulfide. By pulsing the charges and varying the direction and magnitude of the current through the cell, it was found possible to change the resistance reversibly between two stable states. It was also observed that these changes could be accomplished with a few volts, compared to hundreds of volts required by other substances which exhibit bi-stable resistance states, such as nickel oxide.

With the objective of developing, under the program reported herein, a bi-stable resistance element suitable for space applications, studies were made of the procedures for preparing such elements, giving attention to such factors as the composition of the resistive compound, fabrication of the elements, and the nature of the electrodes and the techniques of applying them. With elements prepared in various ways, electrical tests were made to determine the voltages and pulse durations required for their operation, and their reliability in cycling tests; the currents and energies associated with switching were also evaluated. Tests of performance were also made both under exposure and after exposure separately to temperature and vacuum, as well as before and after exposure

to electron beam irradiation. The results of these evaluations are supplemented by comparisons with the performance of nickel oxide and antimony trisulfide, each of which has bi-stable resistance states.

PHYSICS OF SILVER SULFIDE

The β phase of silver sulfide, which is stable below 179° C, is known as argentite. It is monoclinic with the following lattice parameters[2] at 25° C:

a_o: 4.279 Å c_o: 7.862 Å

b_o: 6.931 Å β : 99.61°

The α phase, stable above 179° C, is properly designated as cubic argentite. The two phases differ considerably in the nature of their electrical conductivity, as shown in Figure 1, taken from Hebb[3].

Among the compounds having mixed ionic and electronic conductivity, the monoclinic form of silver sulfide is well known for its very high conductivity; this property of silver sulfide has been the object of investigations extending over thirty or more years. More recently, Miyatani[4] has investigated the polarization of silver sulfide, and Yokota[5] has, in a study of the theory of mixed conduction, made special reference to silver sulfide. These investigations were reviewed by Vendelin[6], with extensive reference to the work of Hebb[3]. Friauf[7] has given a discussion of both ionic and mixed conductivity in crystals and has tabulated parameters for the conductivity equations.

Silver sulfide may be nonstoichiometric. Its conductivity has long been known to depend on its departure from stoichiometry, increasing with increasing silver content, as illustrated in Figure 1. For silver sulfide in equilibrium with sulfur, the transport number for the cation has the unusually high value of 0.99 at room temperature.

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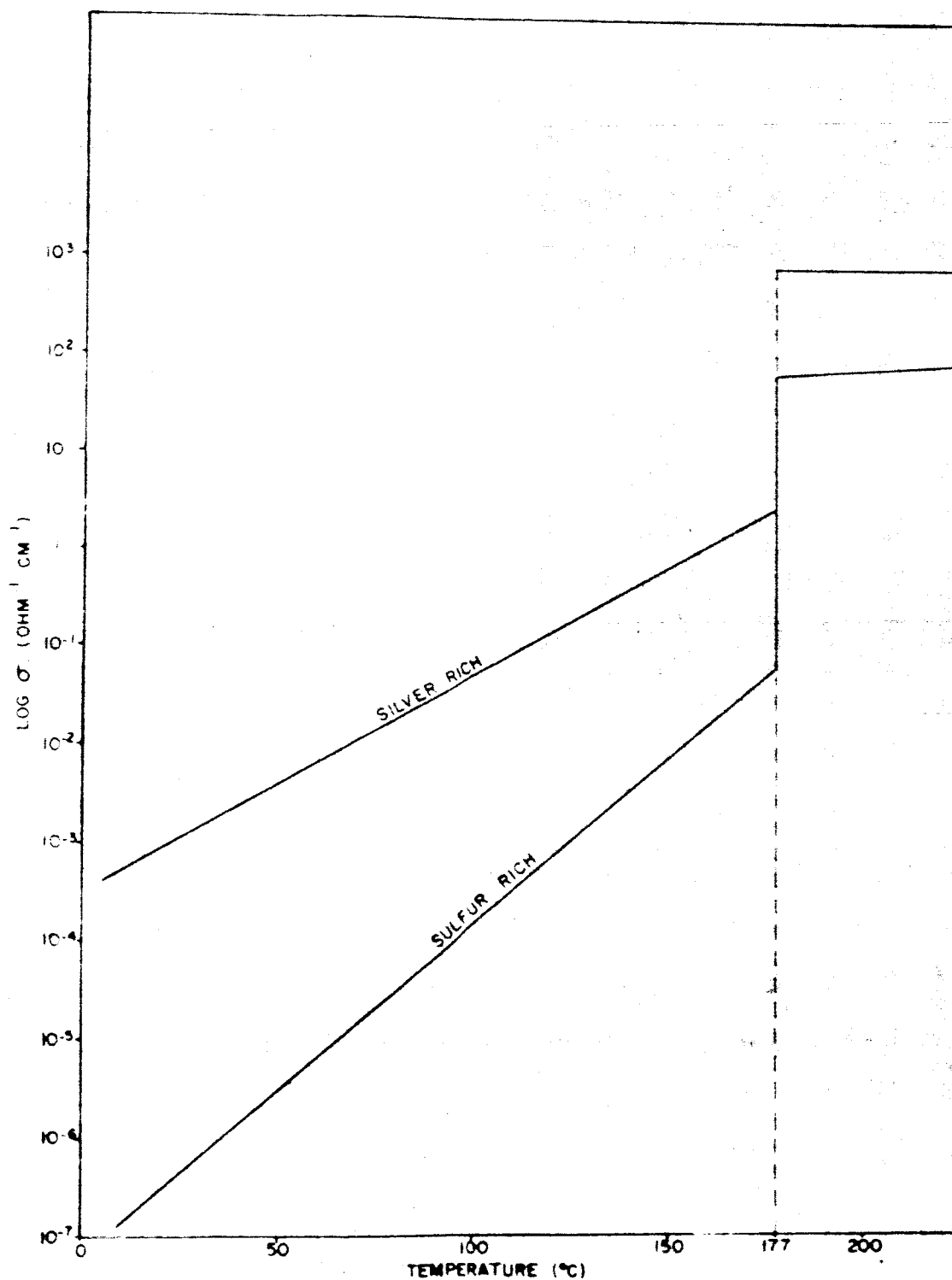
Figure 1. Electrical Conductivity of Silver Sulfide vs Temperature and Composition.

The ionic conductivity may be suppressed by proper choice of electrodes when the applied potentials are less than the decomposition potential of argentite which is about 0.2 v.

CHAPTER II. DISCUSSION

PREPARATION OF THE MEMORY ELEMENTS

The silver sulfide used in making the memory elements for test and evaluation was purchased from the K and K Laboratories, Jamaica, New York, as 99.9% pure, Lot No. 33314. To determine whether a higher purity material would significantly influence the performance results, very pure silver sulfide was prepared by very slowly reacting chemically equivalent amounts of spectrographically pure silver and sulfur in a sealed tube. Tests of the conductivity of a portion of the resulting bole of the silver sulfide indicated that it was most likely slightly silver rich. Tests of the performance of this very pure silver sulfide as a memory element showed that there were other variables in the process of making the elements than the increase of purity obtained with this preparation, and this material was reserved for future tests.

The electrodes of the memory elements usually consisted of platinum and of silver. These metals were of 99.9% purity or better. In the early stages of the work the silver electrode was made from silver powder, while the platinum electrode was in the form of a sheet of foil approximately 0.06 inch in diameter. In the latest experiments, the platinum electrode was also formed from powder.

The pellets for the memory elements were prepared by pressing, using very simple hand-metering devices to provide a measured volume of powder. The procedure finally adopted for making recent silver sulfide memory elements was as follows: (1) Place in the cavity of a 0.25 inch die sufficient silver powder to cover the bottom, press lightly into position by rotating and tapping the plunger; (2) add 55 mg of 100 - 200 mesh silver sulfide from a plastic dispenser, press into position as described above; (3) add about 1 mg of minus 200 mesh platinum powder by means of a plastic dispenser, using a special aluminum funnel to confine the platinum to a 0.05 inch diameter spot at the center of the pellet, press lightly; then (4) complete fabrication of the pellet in a hydraulic press, using 140,000 pounds per square inch. The thickness of the silver

sulfide pellets so prepared is nominally 0.007 inch. Elements formed in this way are sufficiently sturdy to permit any reasonable handling without breakage.

The density of the pellets without electrodes was determined as 7.18 g/cm^3 by pycnometer; this may be compared with a density of 7.234 g/cm^3 determined from measurements of a stoichiometric silver sulfide by the National Bureau of Standards[2].

Preliminary tests were made on silver sheets on which a layer of silver sulfide was formed by immersion in liquid sulfur at about 130° to 140° C for ten minutes to one hour. Thicknesses of the sulfide layer varied from about 0.0003 to 0.0015 inch. The unreacted silver served as one electrode; the other electrode was a piece of platinum foil or platinum wire which was held against the silver sulfide by means of spring pressure.

ELECTRICAL MODEL OF THE MEMORY ELEMENT

The silver sulfide memory element may be electrically represented by the equivalent circuit of Figure 2, where R_{Low} and R_{High} are the true bi-stable resistance values of the active or switching portion of the element. These are dependent upon the input energy and the history of the device. A shunt resistance is added to this equivalent circuit to represent the passive or non-switching volume of the element. This resistance can include such effects as polarization and the deterioration of the electrical or memory capabilities of the silver sulfide element with total operation.

For a given resistivity of silver sulfide, the initial a-c resistance of the memory device before being switched is dependent upon the electrode configuration, the nature of the contact to the silver sulfide, and the characteristic of the compressed silver sulfide. Figure 3 indicates the calculated variation in resistance for a 0.250-inch diameter element comparing a right truncated core, R_{TC}, and a

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V

$R_{LOW} = R(V,T)$

$R_{HIGH} = R(V,T)$

$R_{SHUNT} = R(V,T,\tau,\int dt, - - - - - -)$

V - VOLTAGE

T - PULSE DURATION

τ - ELAPSED TIME AFTER TERMINATION OF PULSE

$\int dt$ - INTEGRATED OPERATING TIME OF ELEMENT
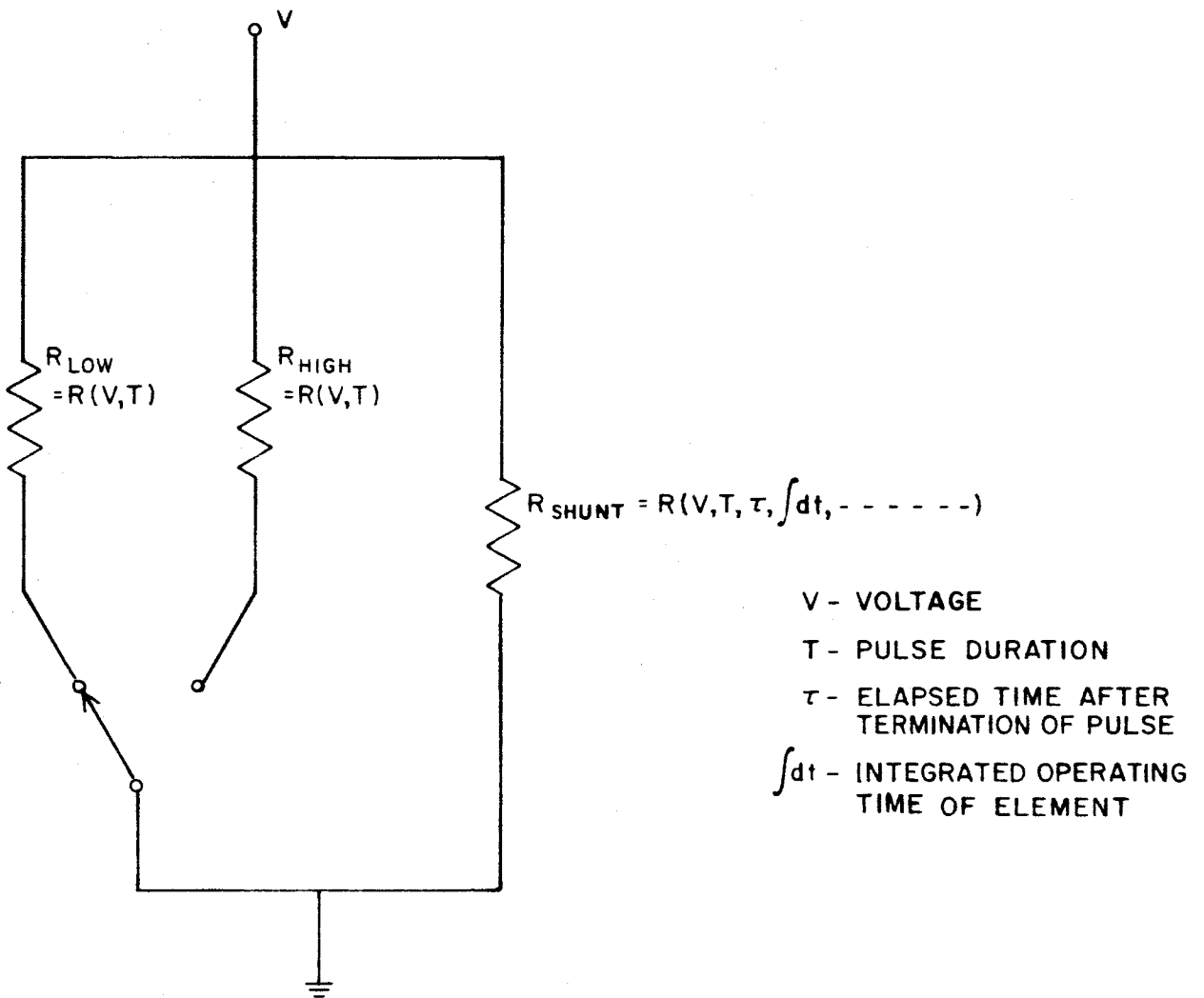
Figure 2. Equivalent Electrical Circuit for a Silver Sulfide Memory Element

$\rho = 730$ OHM-CM (Ag$_2$ S)

$r_1 = 0.125$ INCH (Ag ELECTRODE)

L = DETERMINED BY RADIUS OF Pt ELECTRODE

$$R_{TC} = R_{TRUNCATED\ CONE} = \frac{\rho L}{\pi r_1^2} \left[\frac{L}{L-L_1} - 1 \right]$$

$$R_{RC} = R_{RIGHT\ CYLINDER} = \frac{\rho \ell}{\pi r^2}$$

$\ell = 0.005$ INCH (DISTANCE BETWEEN ELECTRODES)

R_{RC}

R_{TC}

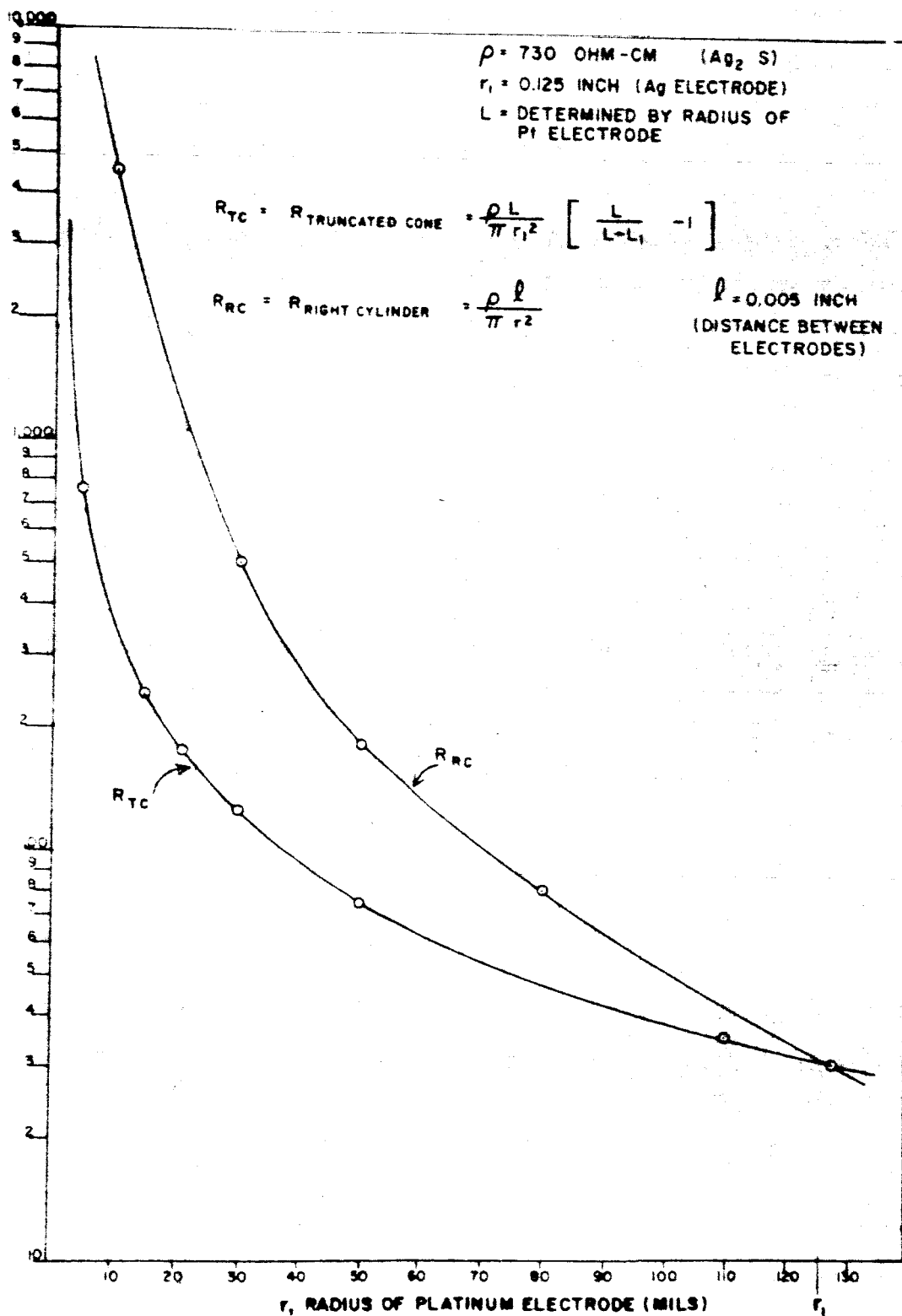r, RADIUS OF PLATINUM ELECTRODE (MILS)

r_1

Figure 3. Calculated Resistance vs Electrode Size

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right circular cylinder approximation, R_{RC}. The derivation of the former is included in the Appendix I. In actuality, an experimental device will have an initial resistance somewhere between these two values or curves.

Depending upon the energy source used in switching, the device may require a negative forming voltage to initiate the breakdown to the low resistance state and thereby commence cyclic operation. The time required for the forming operation varies from practically zero to many seconds depending on the individual element and the applied voltage.

After forming, the switching characteristics of the silver sulfide memory element are polarity dependent, as drawn in Figure 4. Negative voltages applied to the platinum electrode switch the element from a high to a low resistance state; positive polarities restore the element to its high resistance value. This polarity dependence holds for a-c operation as described in the section on Dynamic Switching.

PULSED SWITCHING

Several different energy sources and cyclic devices were applied to the silver sulfide memory element to study its behavior. These are described in the chronological order of their usage.

One of the first employed two magnetically actuated reed relays as illustrated in Figure 5 and Figure 6. A wet battery provided the ± 2.2 v potential applied to the combination memory element and a series 0.75-ohm resistor. Resistances were obtained by measuring both the voltage and the current during the pulses. Sample data obtained by this method are listed in Table I. Resistance values were often an order of magnitude higher than those shown but varied greatly. Usually, the ratio of resistances between the two states was less than 10 and often only 4 or 5, even when measured with an a-c bridge. In all cases, a forming voltage of -2.2 volts applied to the platinum electrode for a sufficient time to

9
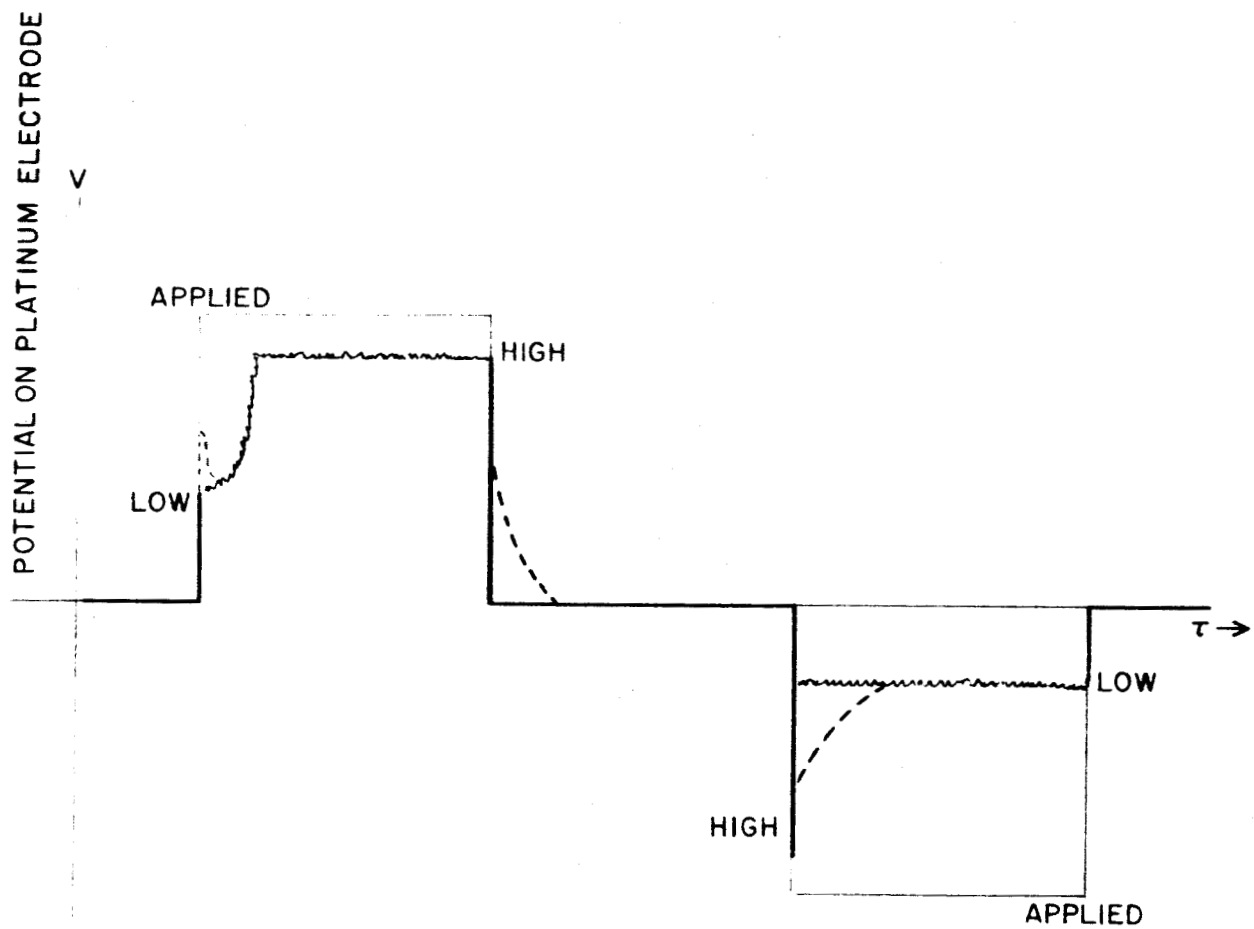
Figure 4. Switching Characteristics for a Silver Sulfide Memory
Element

MAGNET

SLOT TO TRIGGER SWITCH

COLD ROLLEDSTEEL DISC.

MAGNETIC REED SWITCH UNDER THE DISC.
(2 REQUIRED: ONE FOR + AND ONE FOR −)

SWITCH FOR + OUTPUT

STATIONARY MAGNET

SLOT

OUTPUT TERMINALS

+ V
O
− V

STATIONARY MAGNET

TURNS AT II CPS

CHASSIS TOP

SWITCH FOR −OUTPUT

0.75 Ω

PLATINUM

SILVER

REED SWITCHES

+ −

WET BATTERIES
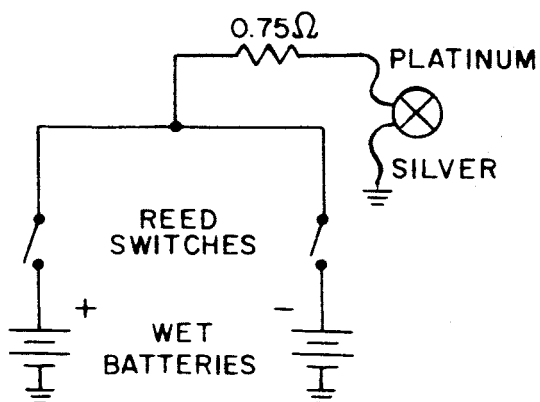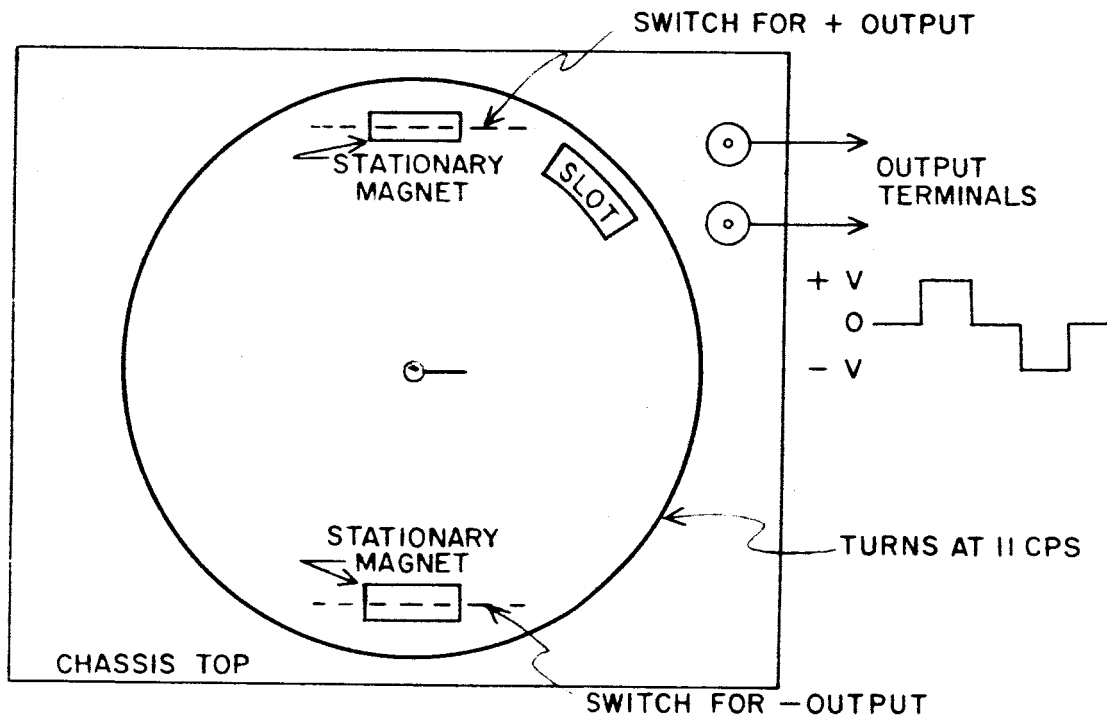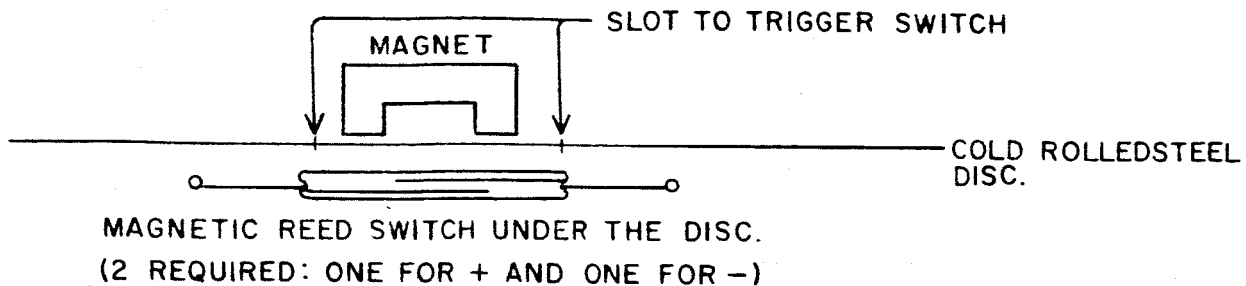
Figure 5. Reed Relay Switching Apparatus

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CRO₁
CURRENT MEASUREMENT

0.75 Ω

Ag₂S
MEMORY
ELEMENT

CRO₂
VOLTAGE
MEASUREMENT

±2.2 VOLTS
10 ms DURATION
90 ms PERIOD
11.1 cps
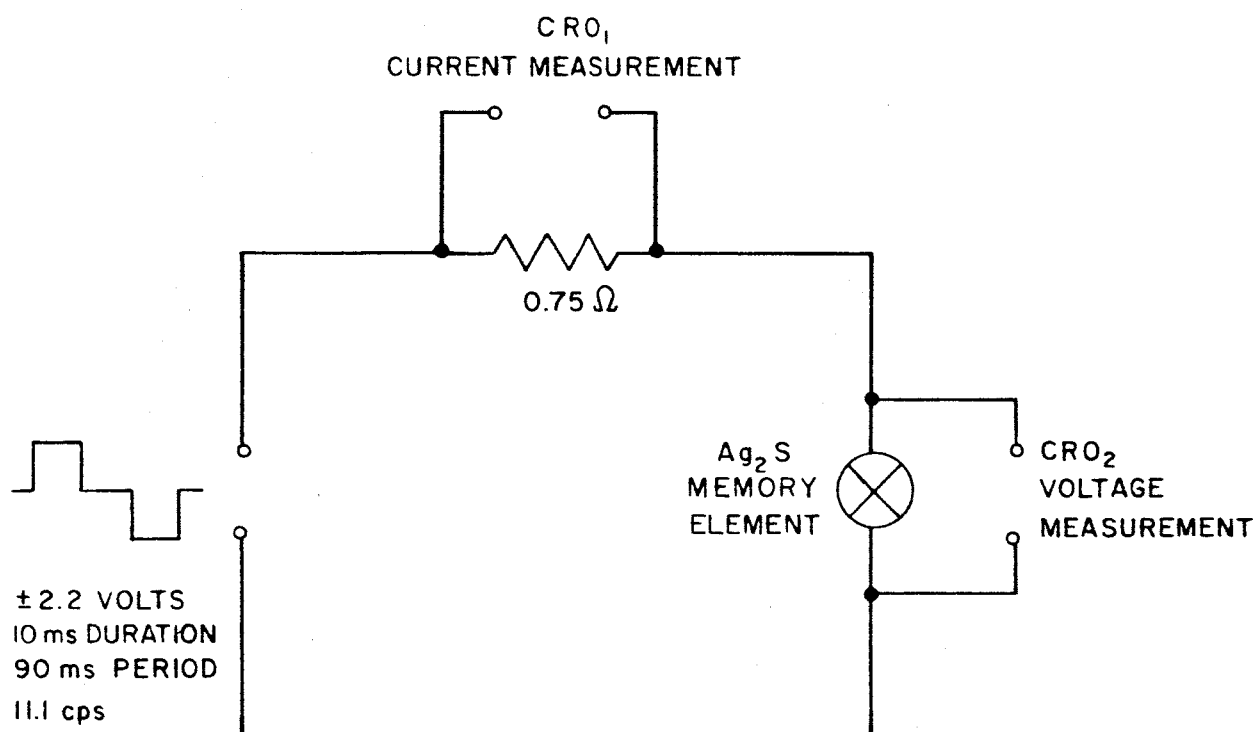
Figure 6.   Reed Relay Switching and Measurement Circuit

TABLE I

Typical Measurements
Reed Relay Apparatus

State	V	I	R
Low	0.7 v	2 a	0.35
High	1.5 v	1.1 a	1.4

Resistance Ratio = 4.0

State	V	I	R
Low	1.5 v	0.8 a	1.9
High	2.2 v	0.2 a	11

Resistance Ratio = 5.8

form the resistive path was required. Tests using this apparatus indicated lifetimes of approximately 3×10^5 cycles until the two states were indiscernible. No attempt was made to record the frequency of failure to switch.

Cycling speeds nearly 10 times faster than the reed relay apparatus were obtained with the mercury relay circuit of Figure 7. A 45-volt dry battery was used to study the behavior of the memory element when operating at higher resistance ratios, and also to observe the dynamic switching characteristics described in the next section. The memory element was connected to the battery through a 10-ohm series resistor. Cycling was discontinued when the ratio of the high resistance to the low resistance decreased to 4. At 100 cycles per second, the lifetime was essentially the same as that measured previously.

Finally, a flip-flop circuit utilizing a silicon controlled rectifier, Figures 8 and 9, was used to obtain most of the switching and cycling data. A typical voltage-current pattern is shown in Figure 16. Again, a 45-volt dry battery and a 10-ohm series resistor were used.

Figure 7. Mercury Relay Switching and Measurement Circuit

Figure 8. Silicon Controlled Rectifier Switching
and Measurement Circuit

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Figure 9a. Silicon Controlled Rectifier Switching and Measurement Circuit

Q1,4,5,6,7,8 = 2N1448
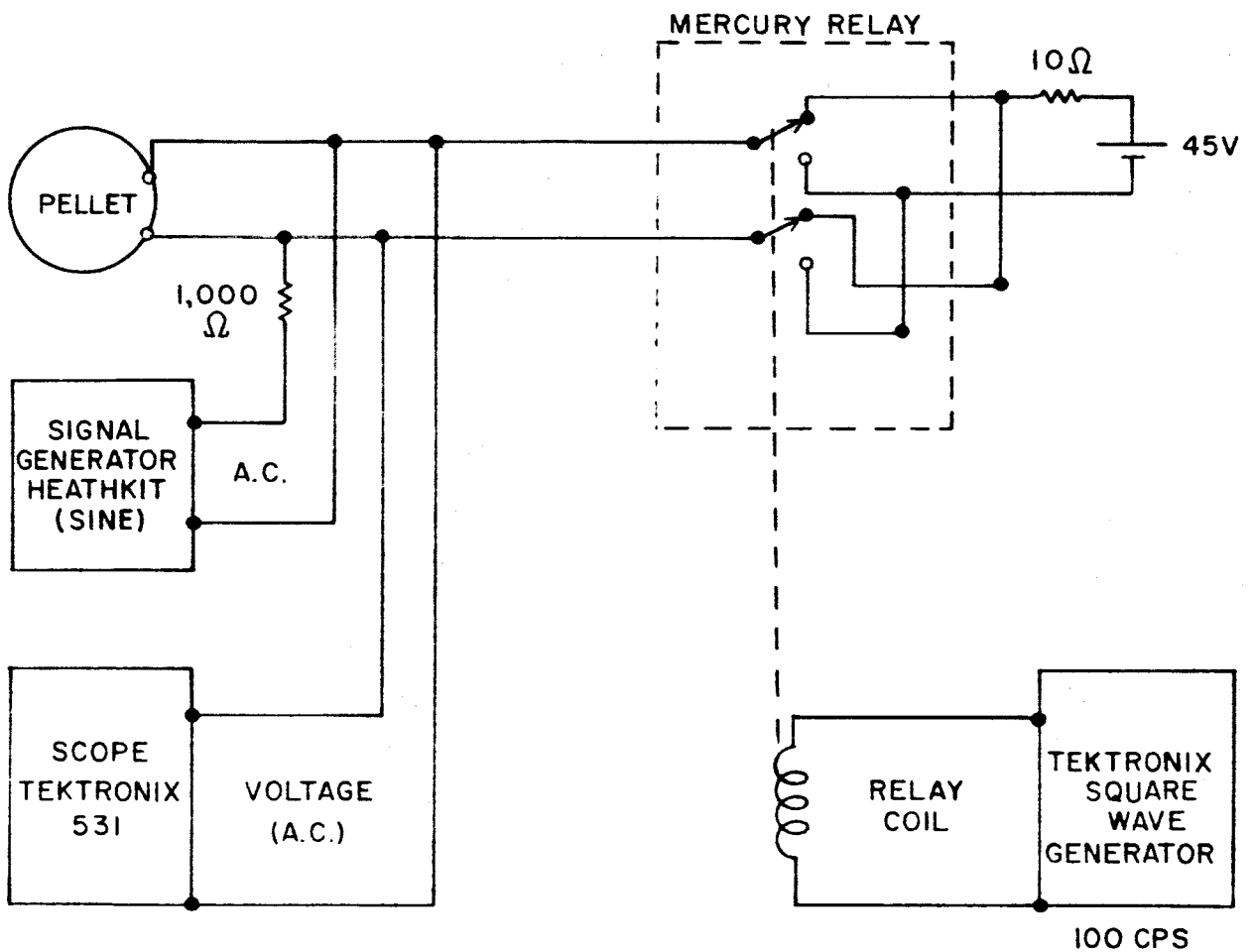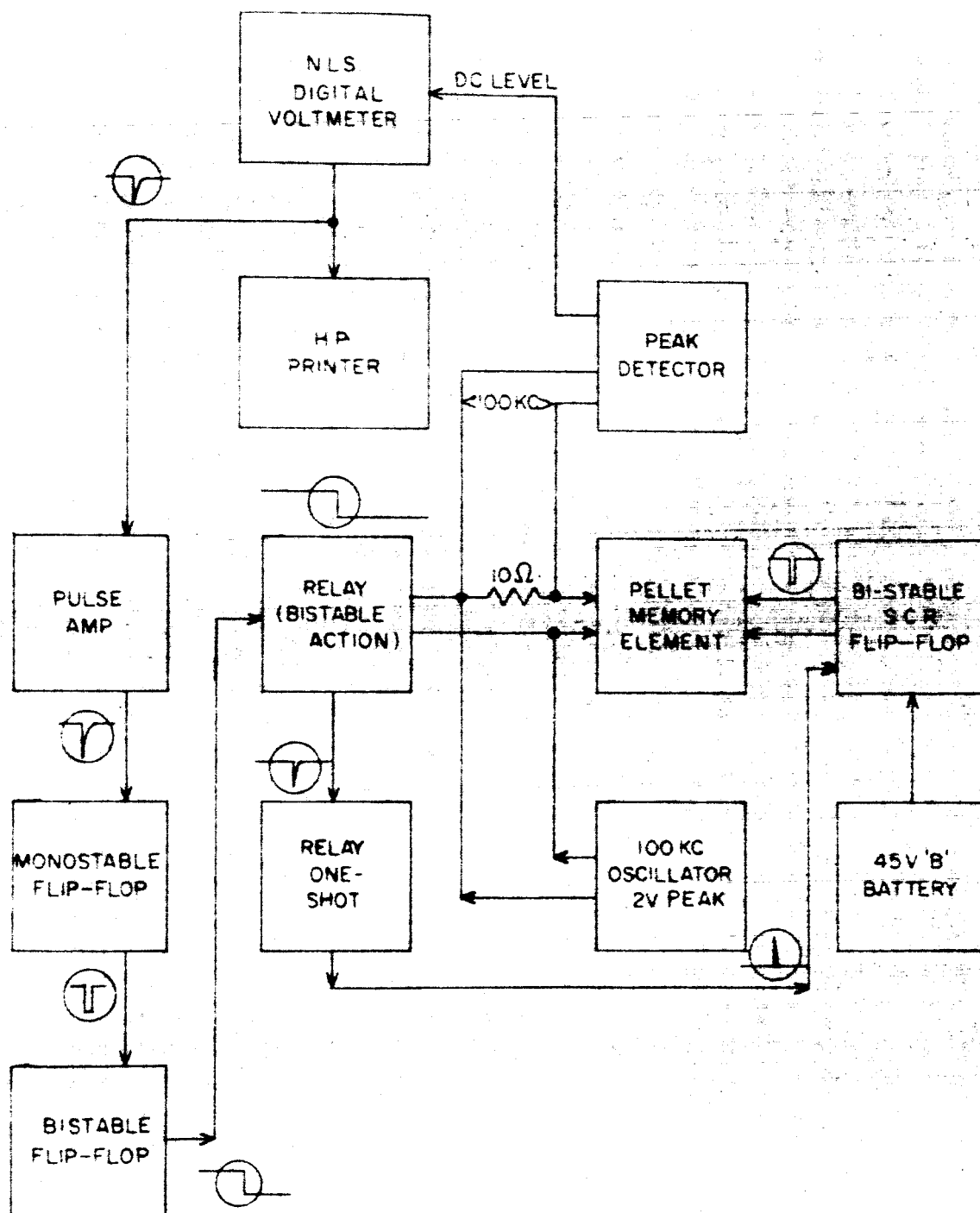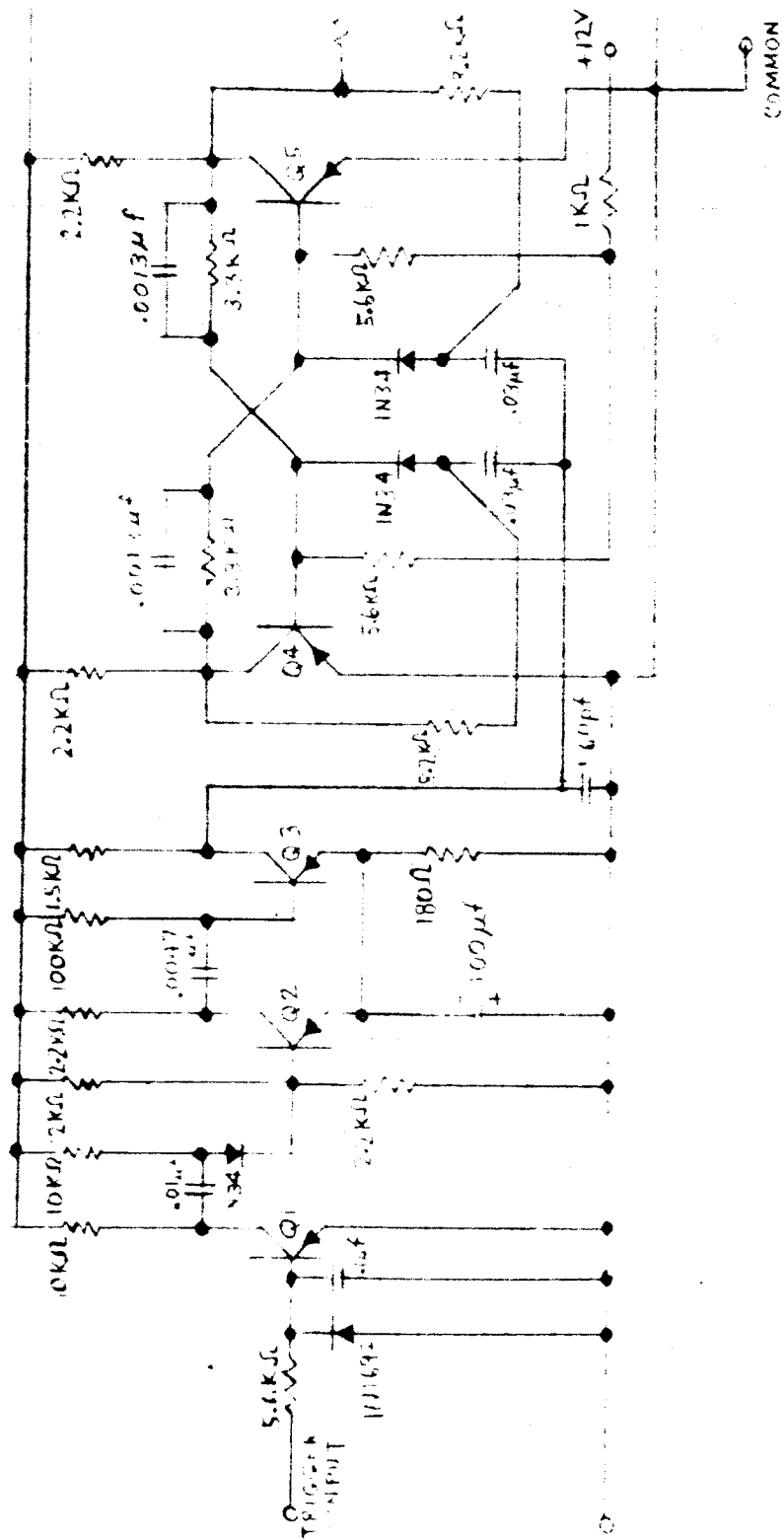Q2,3 = SM15
Q13,14 = 2N1773

C_1 — TIMING CAPACITOR FOR PULSE WIDTH APPLIED TO PELLET

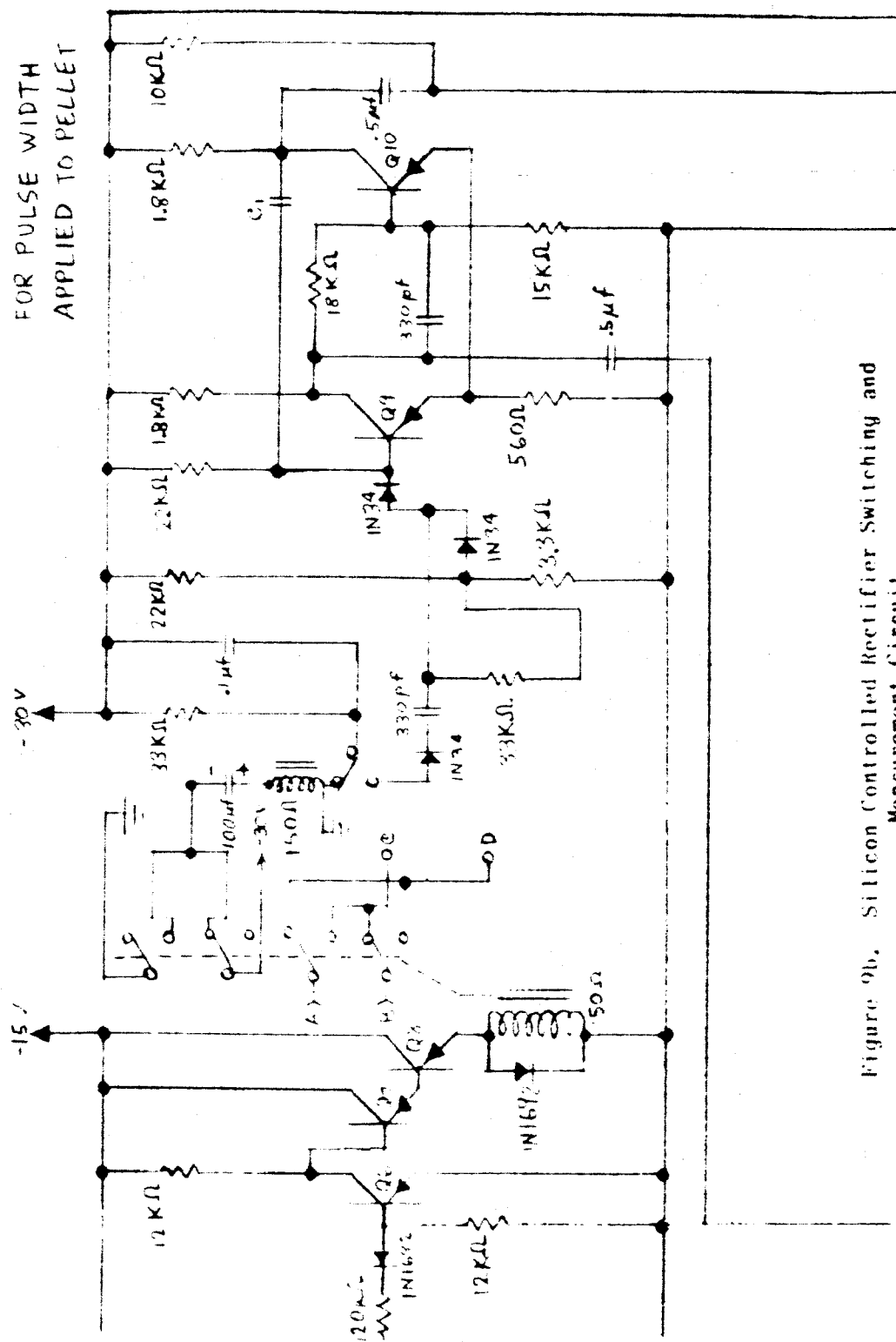Figure 9b. Silicon Controlled Rectifier Switching and Measurement Circuit

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Figure 9c. Silicon Controlled Rectifier Switching and Measurement Circuit
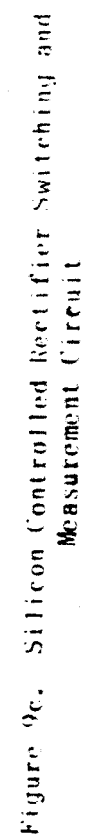
Higher resistance ratios were obtained in this manner, and no forming voltage was required. Three-hundred millisecond voltage pulses could be used. However, improved operation was obtained initially by reducing the duration of the negative pulse; this allowed easier restoration of the high resistance state. Operation using symmetrical positive and negative voltage pulses of 15 millisecond duration appeared to be suitable.

The hysteresis pattern has been used to calculate the order of magnitude of energy required to switch the device. Approximately 1 watt-second was required to switch from 300 to 3 ohms using a 300 millisecond pulse.

A 2 volt peak, 100-kilocycle, half-wave a-c voltage was impressed across the series combination of the silver sulfide memory element and the 10-ohm resistor as a means of reading non-destructively the resistance state between switching pulses. Because of the silicon controlled rectifiers in the switching circuit, the readout signal is essentially half-wave a-c having a positive polarity with respect to the platinum electrode. The voltage across the 10-ohm series resistor was detected and automatically recorded by the digital voltmeter and printer. These data were later converted into the actual resistance of the memory device. The print command signal was utilized to reset the circuit for the following pulse of opposite polarity. Thus, the digital voltmeter and printer, in effect, determined the cycling speed of this means of testing.

This type of readout can be modified to a uni-polar, single-pulse, non-destructive readout system. Brief experiments have shown that a single, 1 volt, positive pulse having a duration of 50 microseconds can be used. It must have a long enough rise time, however, to read in a non-destructive manner as pulses having short rise times will switch the device during readout. The rise time is not yet adequately determined, but is believed to be, very roughly, not less than 10 microseconds.

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DYNAMIC SWITCHING

The slope of a current-voltage dynamic switching characteristic indicates the variation in resistance and the actual switching between the bi-stable resistance states. By displaying such a characteristic with a cathode ray oscilloscope, qualitative information was obtained on the capabilities of the memory device when the operating parameters--such as power, frequency, temperature, and pressure--were changed.

Figure 10 is a typical sinusoidal current-voltage hysteresis pattern. The initial resistances of the high and low states as determined by the slopes of the curve, are 9 and 2.8 ohms respectively. This is representative of low-frequency, low-voltage switching. A switching energy of approximately 10^{-4} watt-seconds has been calculated from this pattern. Arrows on the pattern denote the only direction that it may be traversed for completing a switching cycle. Reversing the direction will result in the traversal of either the low or the high resistance slopes without switching, depending upon the particular state of the memory element. Such a pattern has also been produced manually using a sine-taper potentiometer; this verified these observations as would be expected since this method is merely an alternate means of observing the polarity dependence necessary for switching. With the sine-taper potentiometer, an operating point near the current maximum in the first quadrant of the hysteresis pattern could be maintained for many minutes without the device switching to the high-resistance state. However, a slight increase in current with respect to this operating point immediately changed the state of the device. Likewise, any point on the high resistive branch for negative polarities could also be maintained. The shape of this high-resistive branch of the waveform can be at least partially, if not entirely, attributed to thermal changes in resistance resulting from ohmic heating of the active silver sulfide material. This postulate is discussed further in the section on the effects of temperature.
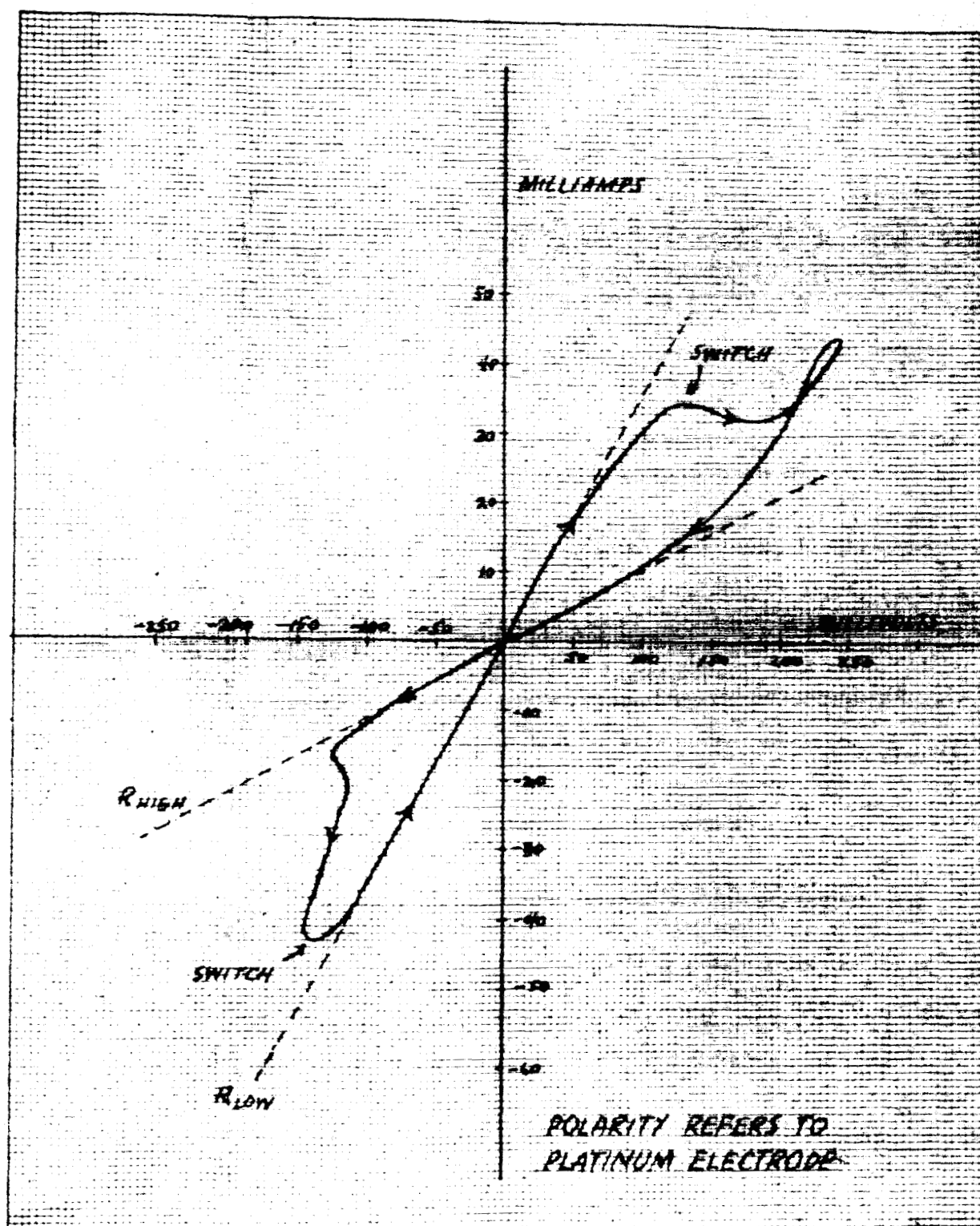
Figure 10. Low—Current Sinusoidal Switching Hysteresis Pattern, 20 cps

Figure 11 depicts the variation of the current-voltage pattern, for a memory element originally in the high resistance state, as the voltage was increased from zero. Initially, for sufficiently low voltages, the element did not switch even though the dynamic slope changed. For slightly higher voltages, the element switched from the high to the low resistance state and cyclic operation commenced. Higher voltages reduced the resistance of the low state still further. Thus, sufficiently low a-c voltages may be used for nondestructive readout of the bi-stable resistive state.

As the frequency was increased, Figure 12, the value of the high resistance state decreased even though the low resistance state remained essentially constant. At frequencies near 70 to 100 kilocycles, there was no apparent switching cycle. This observation led to the use of a 100-kilocycle signal for nondestructive readout with the silicon controlled rectifier flip-flop switching circuit described on page 9. One reason for the unresponsiveness to high frequencies is offered in the section describing the effects of temperature.

The a-c hysteresis for unformed elements was generally similar to those that were formed except that higher potentials were observed-- volts rather than tenths of volts. There were, however, two general classes of patterns that were most often seen, as shown in Figure 13. After forming a low resistance, the memory elements gave similar patterns to that previously described. Figure 14 indicates that this may have been a consequence of using a sheet platinum electrode as there was a dependence associated with the pressure applied directly to this electrode. This observation led to the replacement of the sheet platinum electrode by a powdered electrode of the same material, as described on page 3. This change in the fabrication of the pellet was made near the end of the final period of the contract, and time was no longer available to test elements so made as thoroughly as those made with the sheet platinum electrode. However, it was observed

LOWER RESISTANCE
IN LOW STATE

SWITCHING

HIGH STATE
NO SWITCHING
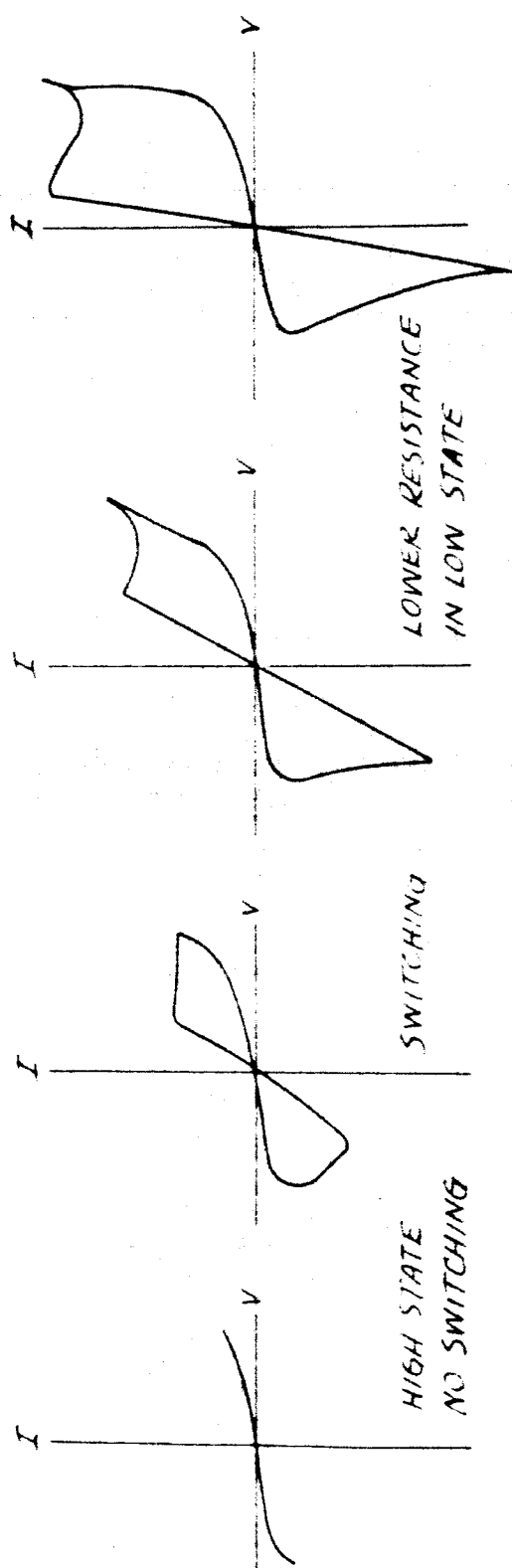
INCREASING VOLTAGE SEQUENCE ⟶

POLARITY REFERS TO PLATINUM ELECTRODE

FORMED ELEMENT

20 CPS

Figure 11.   Effect of Increasing Voltage on
Hysteresis Pattern.

23
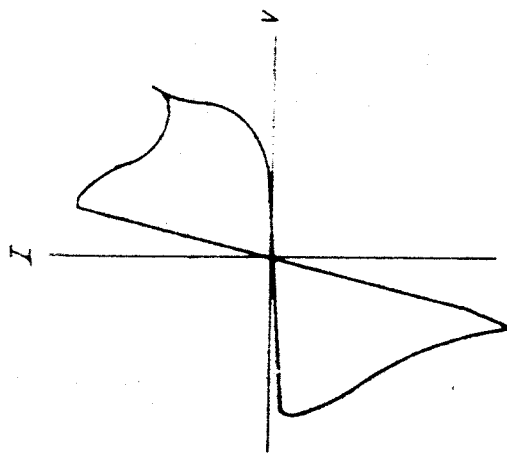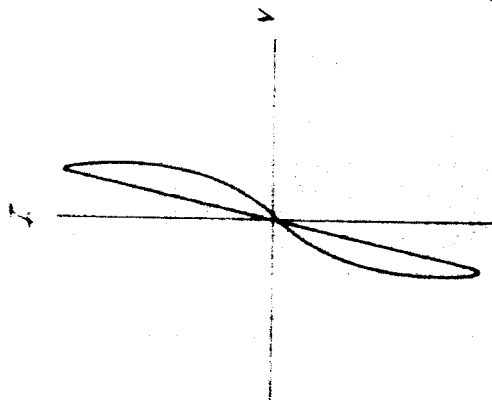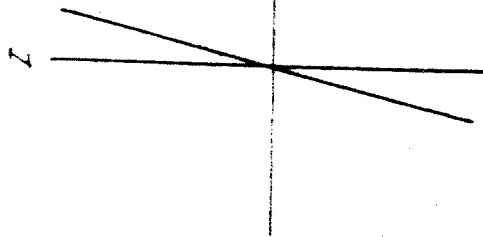
100 KCPS

50 KCPS

20 CPS

POLARITY REFERS TO PLATINUM ELECTRODE

FORMED ELEMENT

Figure 12. Effect of Increasing Frequency
on Hysteresis Pattern

24
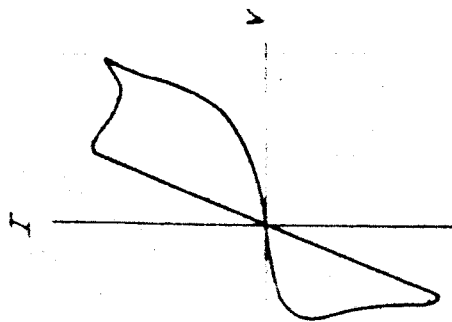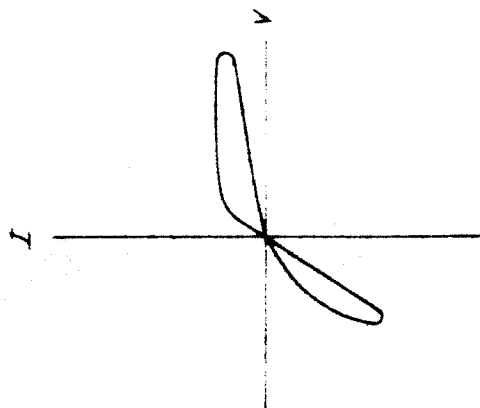
TWO GENERALLY OBSERVED PATTERNS

POLARITY REFERS TO PLATINUM ELECTRODE

20 CPS

Figure 13. Hysteresis Patterns for
Unformed Elements
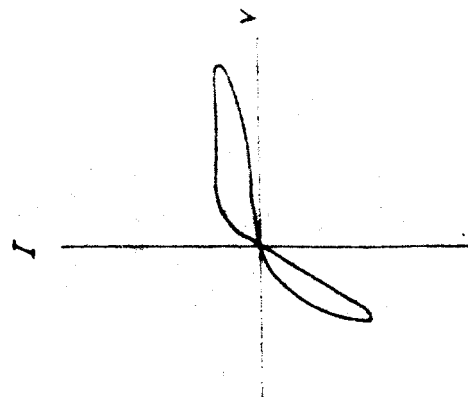
25

INCREASED PRESSURE

V

I

AS MADE

V

I

POLARITY REFERS TO PLATINUM ELECTRODE

20 CPS
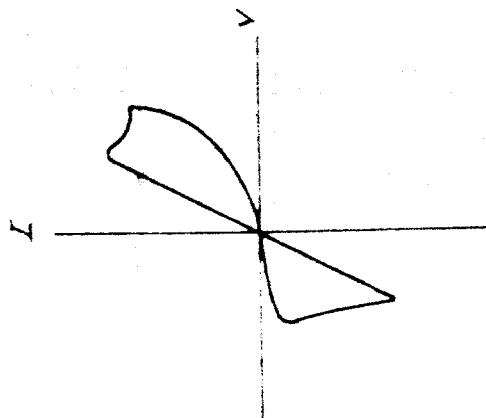
UNFORMED ELEMENT

Figure 14. Effect of Pressure on Platinum
Sheet Electrode of Unformed Element

in making fifty memory elements by this changed fabrication that variations in the pre-forming resistances were significantly less than with the sheet platinum electrode. An unformed unit could also be assisted into switching with the application of heat, Figure 15.

A somewhat different current-voltage relationship was noted when square voltage pulses were used for switching rather than a-c. Pulses are the preferred means for switching the silver sulfide, and a hysteresis pattern so obtained is shown in Figure 16. With power levels much higher than for the previous a-c example, the two states were 280 and 3.3 ohms. This type of hysteresis pattern was likely caused by the inability of the device to respond thermally to the fast rise time of the square voltage pulse applied to it; thus, the high resistance value had less tendency to decay to a lower value as with the a-c operation.

CYCLING TESTS

This section presents results of the switching and cycling measurements made with the test equipment described under the heading PULSED SWITCHING. Data in the form of graphs are presented for normal memory elements. Two types of graphs are included: (1) a record of the resistive values for successive pulses from the initial operating time until the first failure; (2) a chart obtained by sampling every 20 cycles or pairs of pulses (i.e., pulses 1 and 2, 40 and 41, etc.) and thus establishing the lifetime trend of the device. Figures 17 through 20 present such data for the normal memory elements. Elements for this purpose were selected from that group of elements which had gone through all the operations of the radiation test as described in a subsequent section, but which had not been exposed to irradiation but instead being isolated and protected therefrom. The data from one of these selected elements are shown in Figures 17 and 18. The initial failure occurred at the 73rd successive pulse; 5.7% of the first 122 switching attempts likewise did not succeed. The 20,000-ohm

27

COOL

HOT

I

V

POLARITY REFERS TO PLATINUM ELECTRODE

20 CPS

UNFORMED ELEMENT

COOL
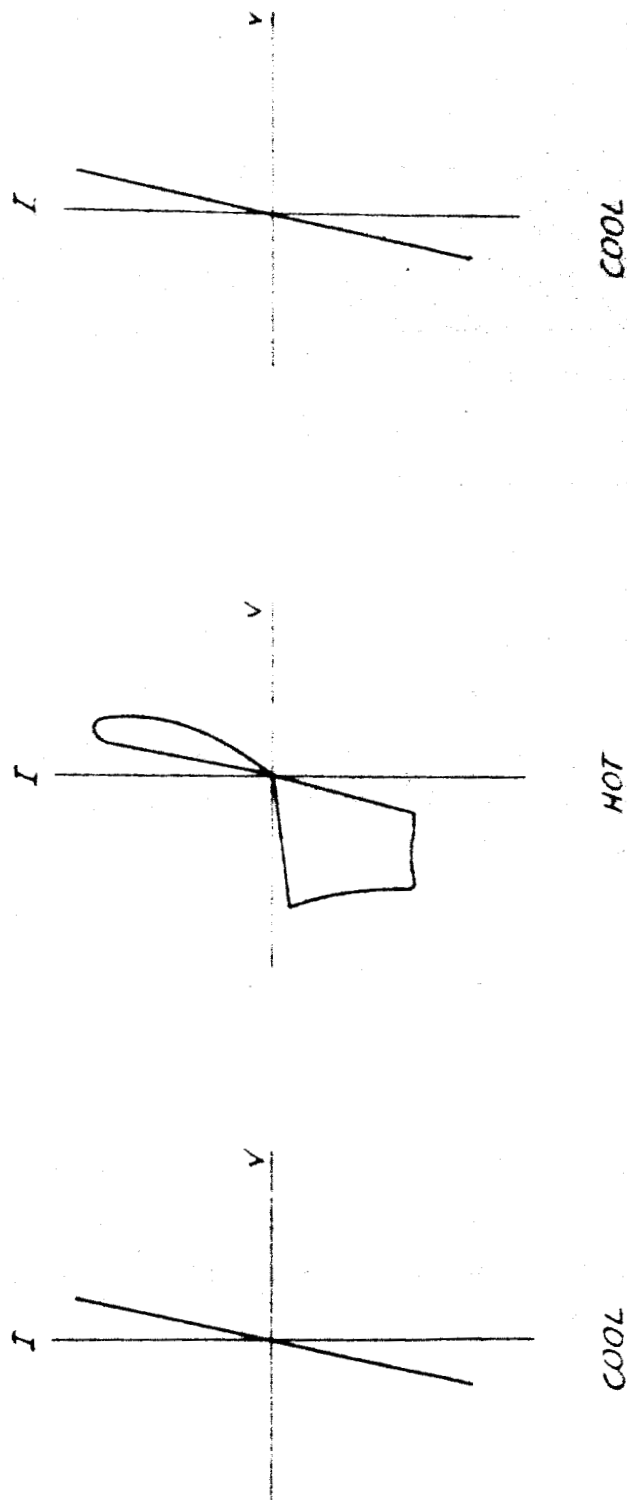
Figure 15. Effect of Increased Temperature on
Hysteresis Pattern of Unformed Element
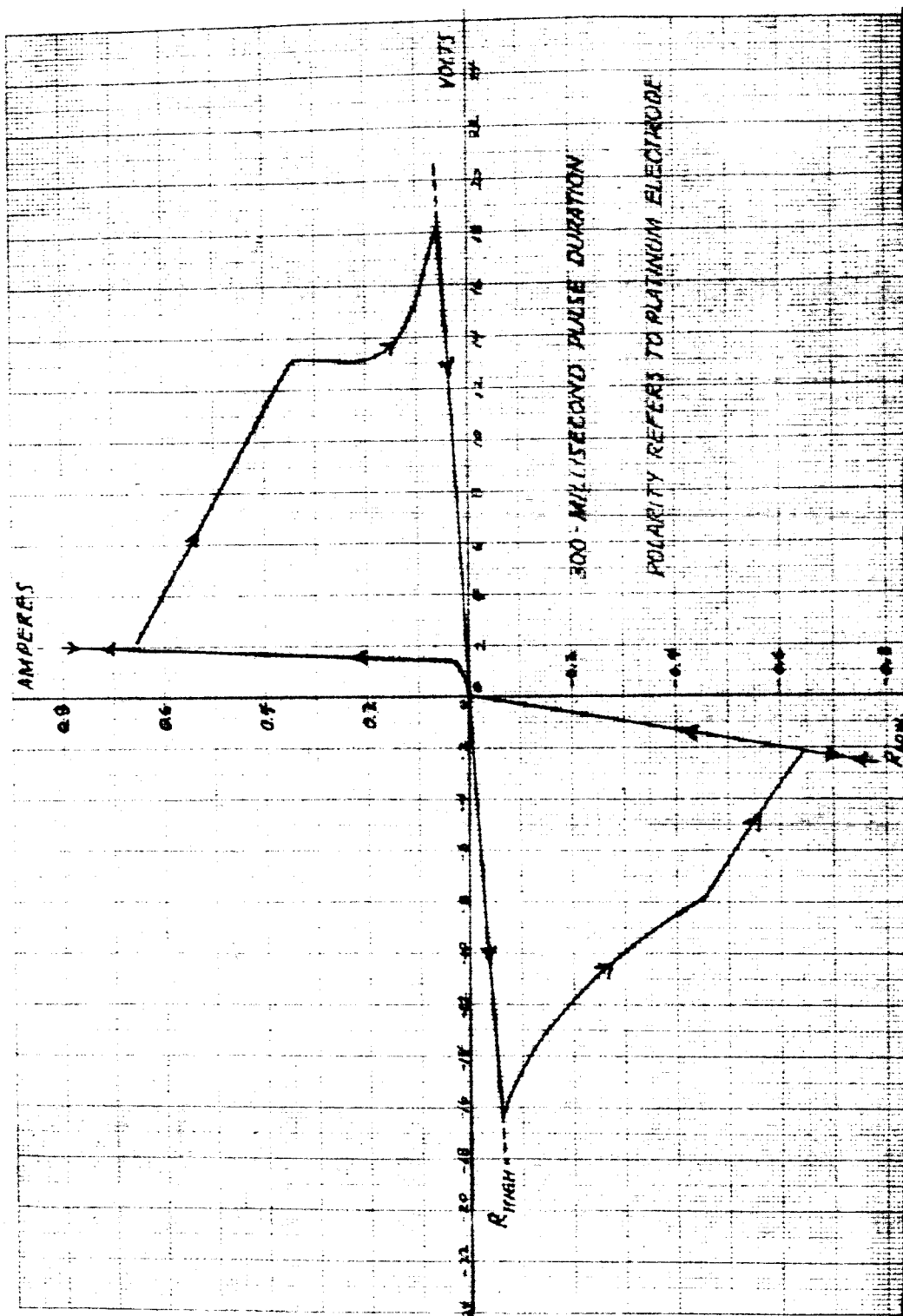
Figure 16. Square-Wave Switching Hysteresis Pattern

29

Figure 17. Initial Switching Data for Typical Element, Group V

CONTROL PELLET GROUP # ⅴ

APPROXIMATE HIGH STATE

HIGH STATE

NUMEROUS FAILURES GTC

LOW STATE

SHORT REST
½ HOUR

CYCLES, × 20

Figure 18

31

Figure 6. Sampled Cycling Data for Typical Element 1

32
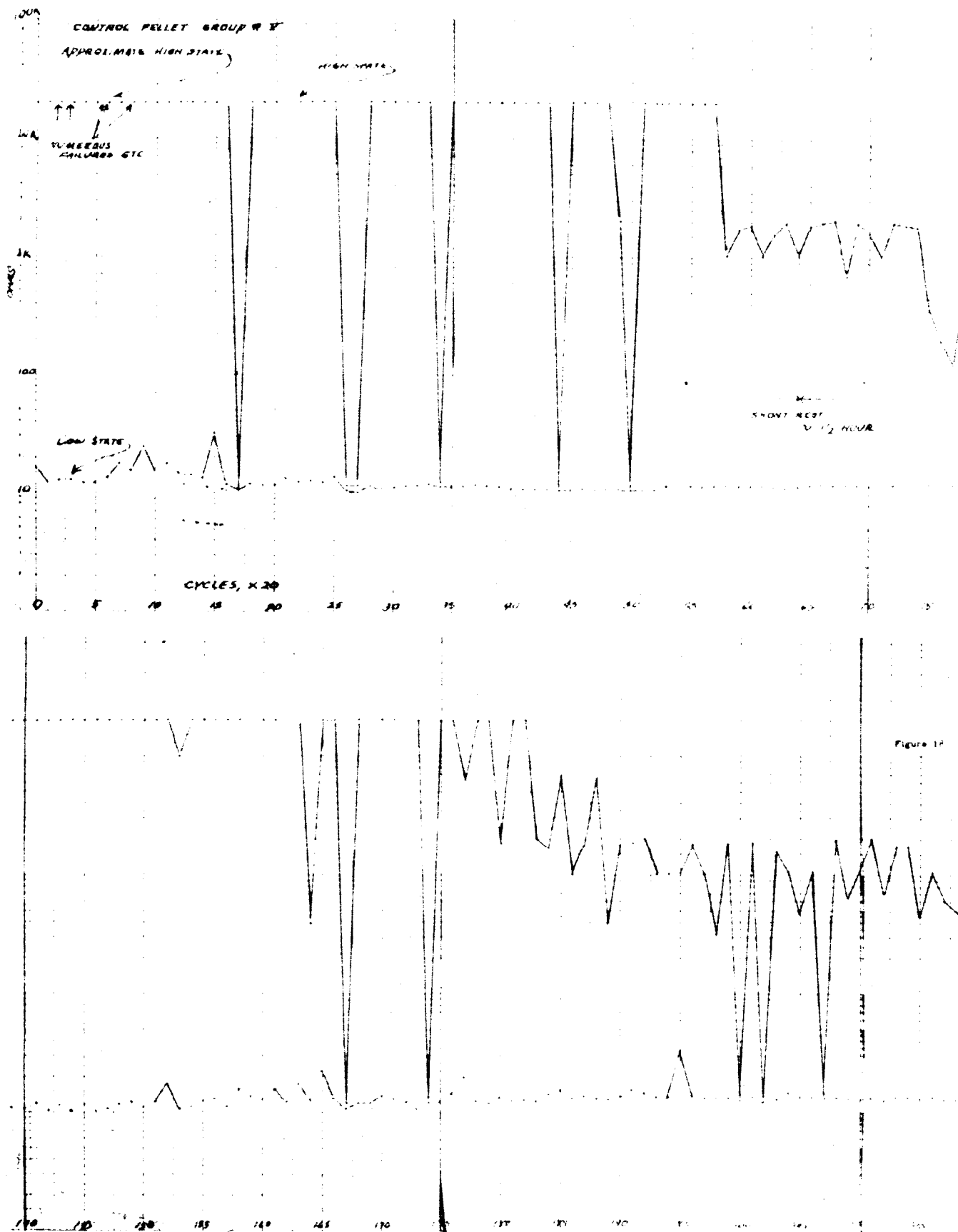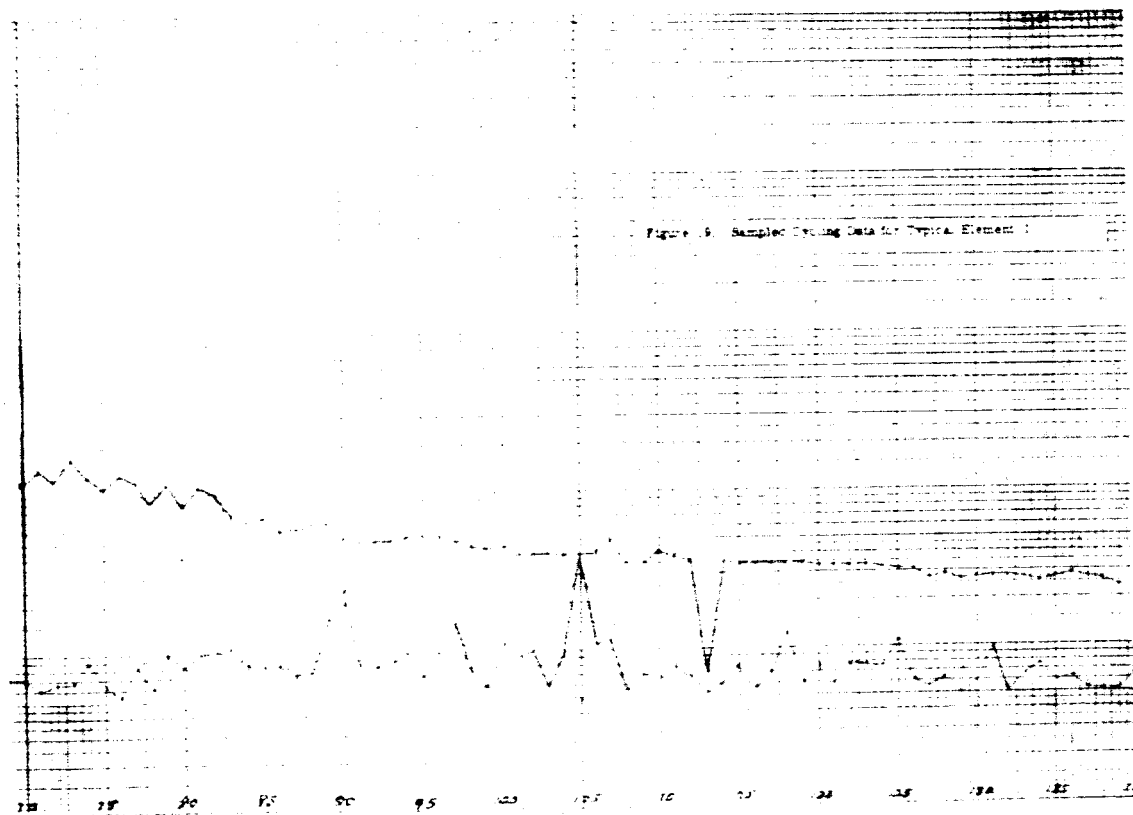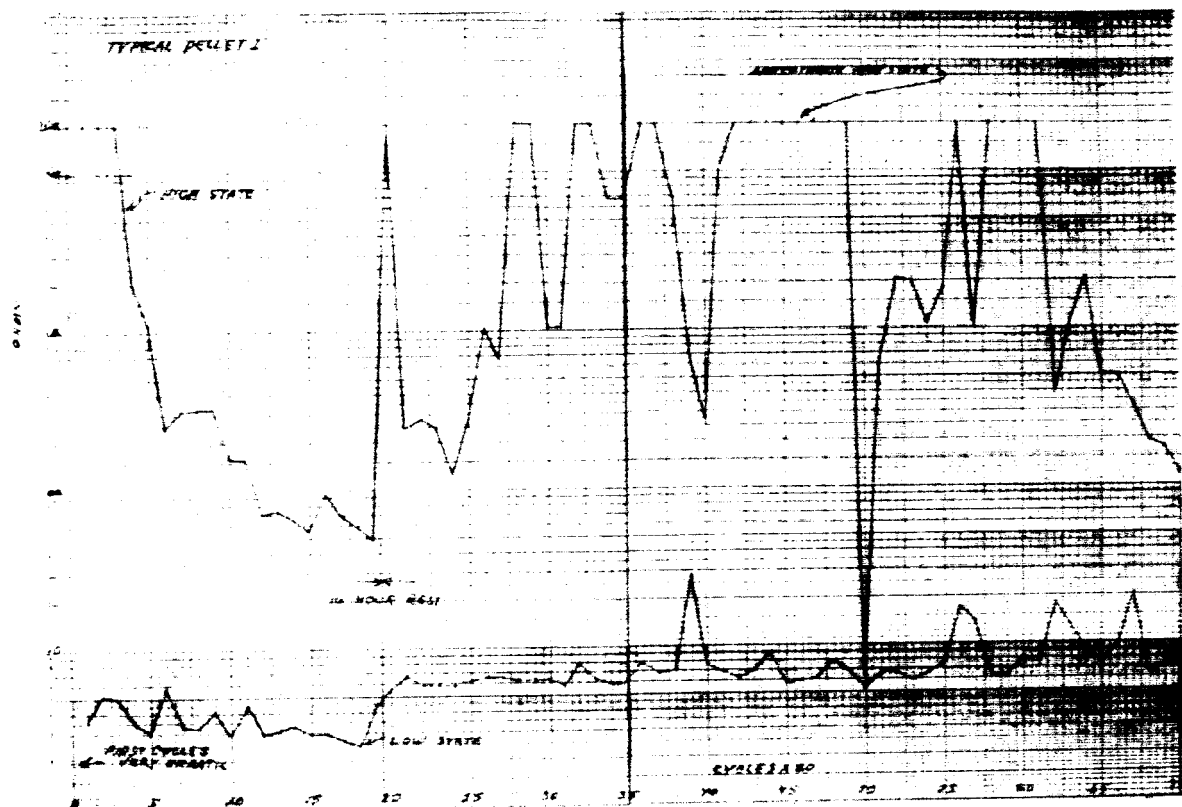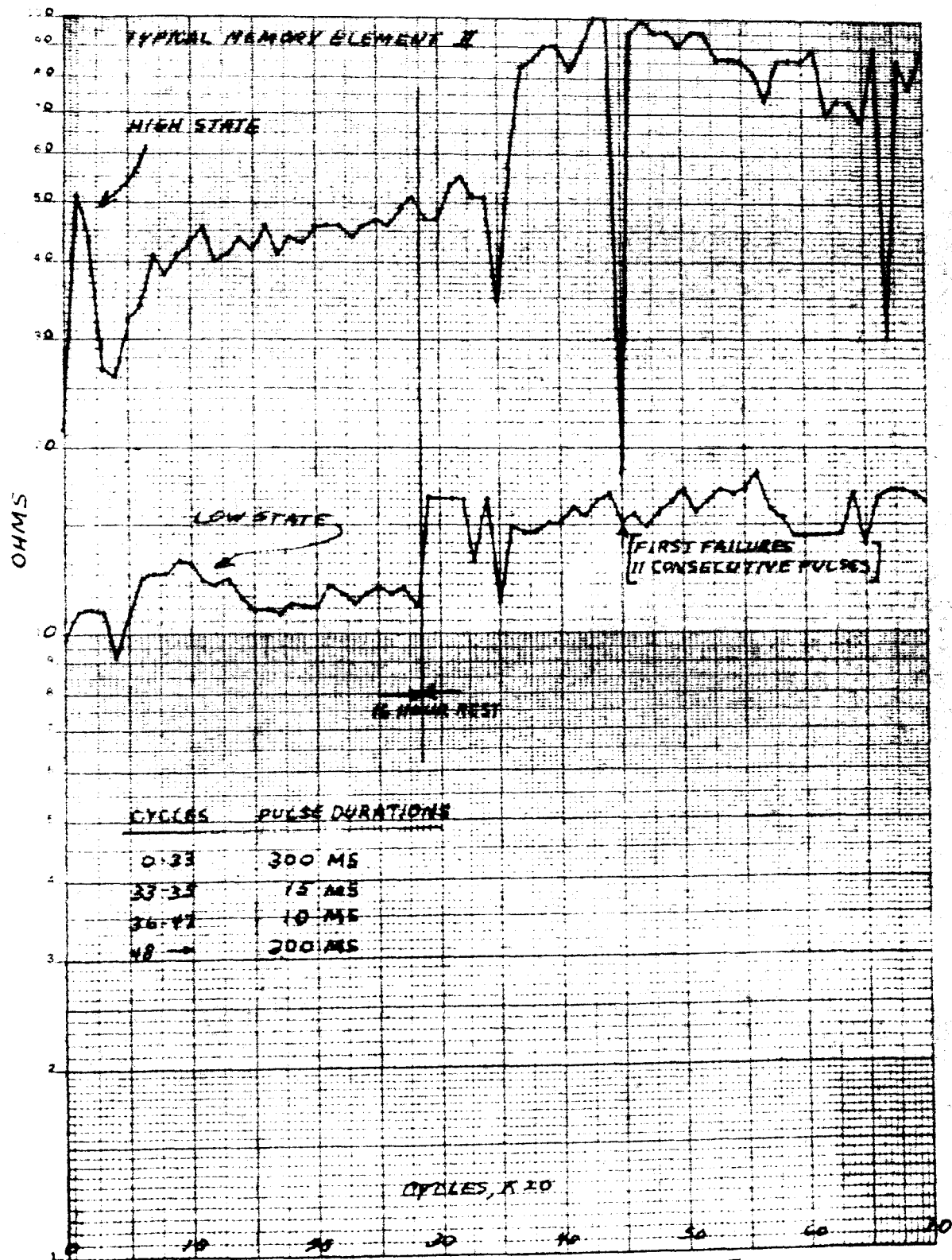
Figure 20. Sampled Cycling Data for Typical Element. II

value for the high resistance state is the upper limit of the sensitivity of the test circuit, and the actual value may be much higher. Initial resistance ratios of approximately 2000 are seen to decay to around 100 with increased operation, and then to return to the original value before finally decaying ultimately to the value of about 5.

A much shorter lifetime was exhibited by a similar element which accompanied the radiation test but was not irradiated, Figure 19. More erratic behavior is also apparent, both initially and throughout its operating life. A portion of the characteristics for a third element, Figure 20, seems to indicate, as previously noted, that initial pulse durations of 300 milliseconds, at least for the negative pulse, are not satisfactory. Shorter duration pulses yielded somewhat higher resistance values for the high state although the maximum value is nearly 200 times less than those of the two previous examples.

The deterioration of the ratio of resistance values for the bi-stable states with total operating time has been shown to be due primarily to a reduction of the high resistance state, the low state remaining essentially stable. Another form of aging was also observed, especially when using the circuit employing the magnetic reed relays rather than the silicon controlled rectifier. This appeared as a delay in switching from the low to high resistance state during the application of the positive voltage pulse. Eventually, this delay equalled or exceeded the duration of the pulse, and the device remained effectively at its low value.

The development of the technique for preparing memory elements with the platinum electrode formed from powder was completed too near the termination of this investigation to permit valid cycling tests on such elements.

THERMAL EFFECTS IN CYCLING

The β form of silver sulfide, being a semiconductor, exhibits a negative temperature coefficient of resistance. This influences the resistance values of a memory element, particularly the high state, as the temperature

34

varies. It also contributes to the actual switching characteristic as
well. The equations governing the conductivity of silver sulfide are
given by Friauf[7]; Figure 21 is a plot of the resistivity with respect
to temperature for silver-rich and sulfur-rich silver sulfide.
Miyatami[2] indicates that a conductivity-temperature hysteresis is also
found for silver sulfide. In both cases, the magnitudes depend greatly
upon the deviations from stoichiometry of the particular silver sulfide
sample.

These variations in resistivity as a function of temperature give
a clue to at least a portion of the switching mechanism. An a-c voltage
current hysteresis was described in the section on Dynamic Switching.
We offer an interpretation of the behavior of the memory element in the
high resistance state in terms of a self-heating thermistor analysis[8];
such an analysis has been applied to the inverse voltage characteristics
of a point contact diode by Hunter[9]. Figure 22 shows a thermal equili-
librium model for the third quadrant of a low frequency switching cycle.
This is based upon the self heating of the silver sulfide and its re-
lated change in resistance. Even though the drawing is approximate, it
clearly shows the effects observed experimentally. For increasing input,
the resistance continues to change and the thermal equilibrium point also
changes. This model assumes that the active material has a very small
volume and can respond rapidly to temperature changes. As the frequency
of operation increases, the temperature of the silver sulfide pellet
increases and the initial value of resistance in the high state thus
decreases. Finally, for a high enough operating frequency, the temper-
ature is so high that the resistance appears essentially to be in the
low state. Such a model has also been postulated mathematically by
G. L. Pearson[10] whose Technical Memorandum has recently been made avail-
able to us. The switching characteristic for square pulses has been
shown to be markedly different than that obtained with sinusoidal wave-
forms. This can be attributed to a lack of thermal equilibrium; hence,
a different voltage-current pattern would be expected.
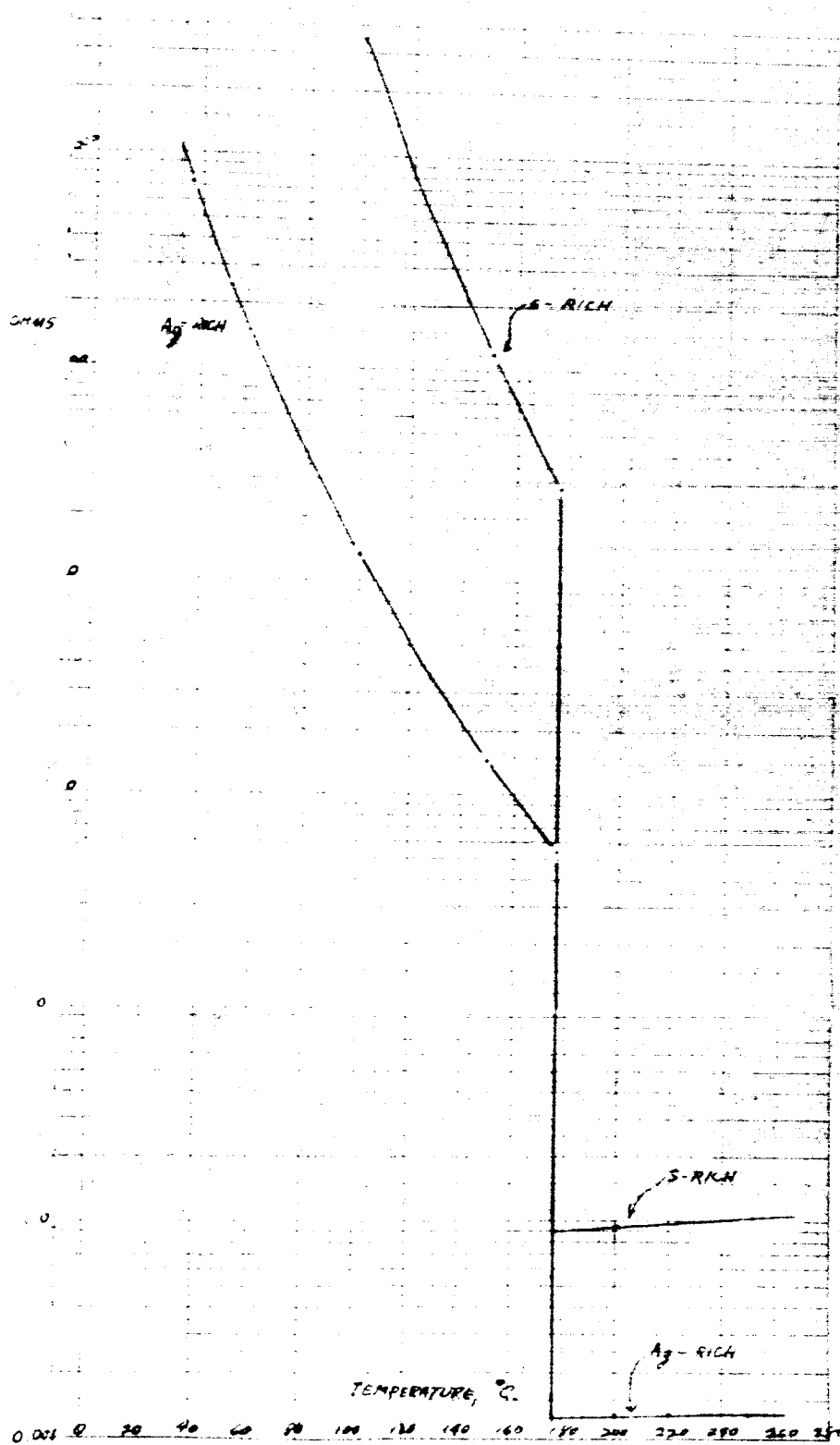
Figure 21.   Resistivity of Silver Sulfide vs Temperature

36
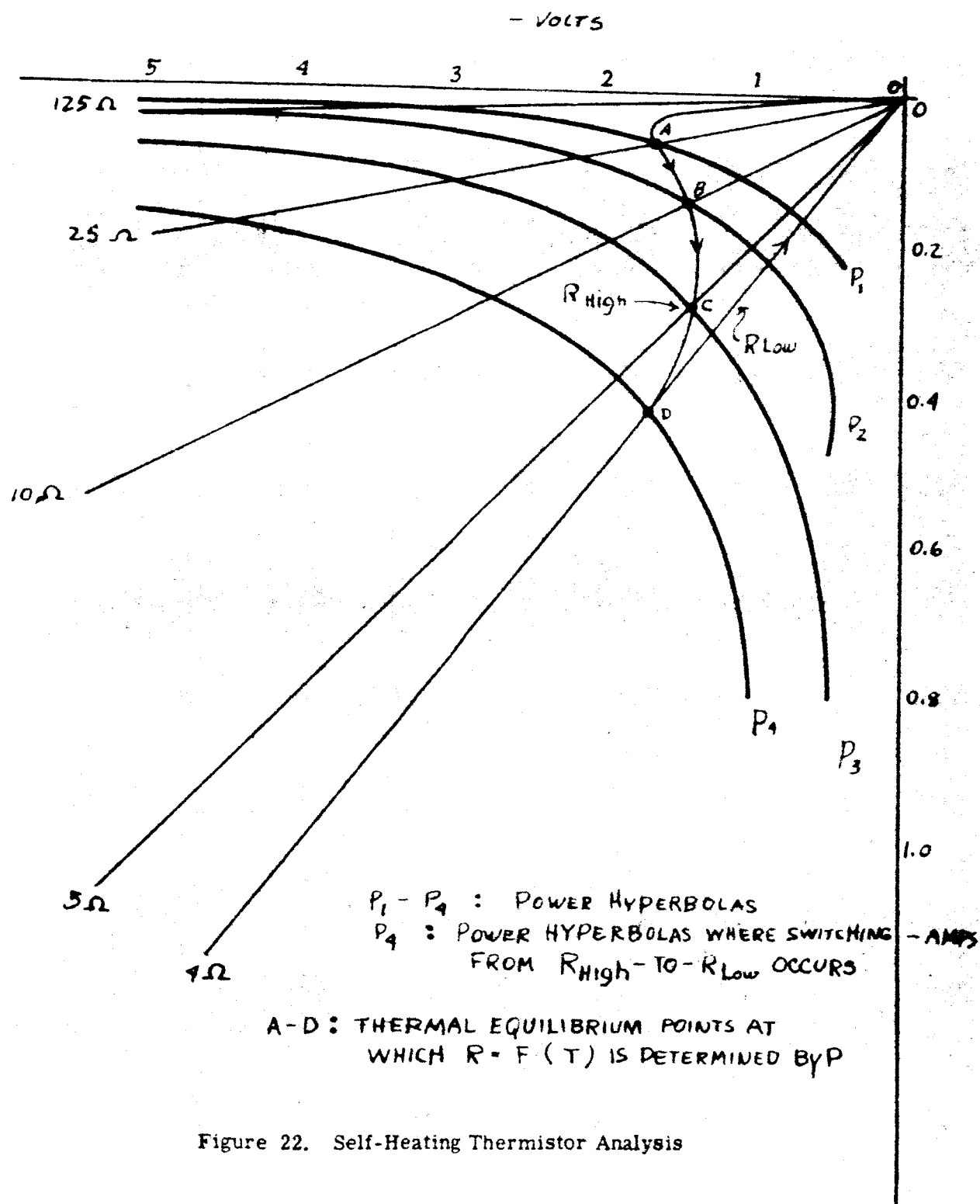
Figure 22.   Self-Heating Thermistor Analysis

The first quadrant of the hysteresis pattern might be explained in a similar manner--this time for a thermistor that is cooling to ambient temperature after being switched to the high state.

This model for the transition from the high to low resistance state does not attempt to explain the actual latching properties of the switch. It does account, though, for a portion of the switching cycle and some of the variations found in the hysteresis effect.

The dependence of the resistivity upon the deviation from stoichiometry will account for many of the differences in resistances from cycle to cycle and element to element. The input power for each pulse used for switching will influence the temperature response of the active silver sulfide material, and likely change the concentration of silver or sulfur in the material near the switching path and thus the total resistance of the memory element.

Qualitative observations of the switching operation at elevated temperatures indicated that less energy is required than at lower temperatures. On the basis of the model just proposed, this would be expected.

EFFECTS OF ENVIRONMENT

Radiation tests were made to obtain an indication of the probability of the silver sulfide memory elements surviving in the space environment. Twelve silver sulfide memory elements were exposed to a 2.0 Mev electron beam from a Dynamatron at the Boeing Company's Aerospace Division. While the entire report from Boeing is reproduced in Appendix II, the pertinent features of the test are summarized in Table II.

Of the twelve elements irradiated, six were in the low resistance state prior to the test; the remainder, in the high state. Each of the two groups were further subdivided so that either the silver or platinum electrodes were toward the beam.

TABLE II

Radiation Test Data

Integrated Electron Dose:

-or-
$$3.0 \times 10^{-8} \ (+10\%, \ -5\%) \ \text{amp-hrs/cm}^2$$
$$2.8 \times 10^7 \ \text{r} \ (\text{Co}^{60} \ \text{equivalent})$$

Time for Irradiation:

834 Seconds

Average Irradiation Rate:

$0.13 \ \mu\text{a/cm}^2$

Temperature Rise:

Negligible; less than 2° C

Incident Electron Energy Spectrum:

2 Mev $\pm$ 0.3%

A comparison of the resistances before and after the irradiation is shown in Figures 23 and 24. All of the memory elements that were originally in the low resistance state were shielded by 63.3 mil thick aluminum during the exposure; they either remained unchanged or were increased in resistance by the irradiation. These elements originally in the high resistance state were unshielded during irradiation; they also changed in resistance. However, the direction of change depended upon the orientation of the memory element in the electron beam. Units having the platinum electrode towards the beam decreased in resistance. With the silver electrode towards the radiation, the units increased in resistance. While the high-energy electron beam is the primary source of radiation, high-energy x-rays were undoubtedly generated by the electrons striking the aluminum shield as well as the elements themselves. It is reasonable to

2 MEV ELECTRON BEAM

Ag
Ag₂S
Pt
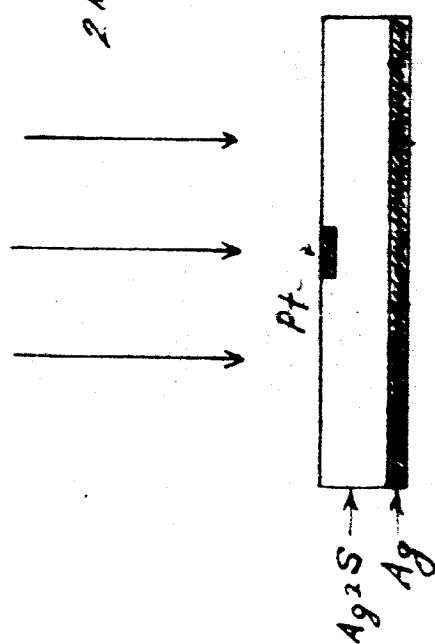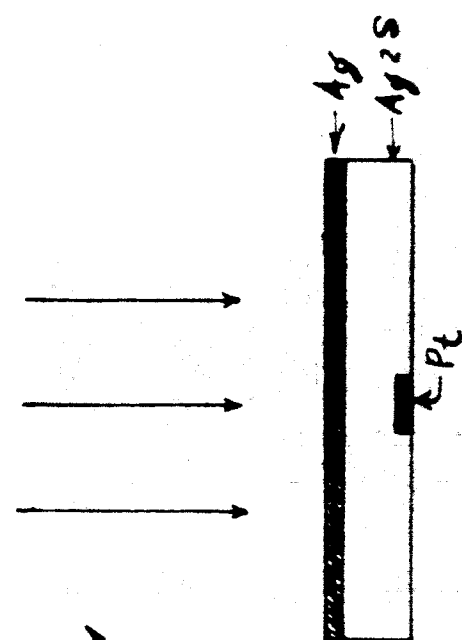
ELEMENT #	RESISTANCE ORIGINAL	FINAL
G-10	9.7	13.5
G-11	10.6	14.0
G-12	45.0	52.5

DATE OF MEASUREMENTS
ORIGINAL 10-5-63
FINAL 10-30-63

Pt
Ag₂S
Ag

ELEMENT #	RESISTANCE ORIGINAL	FINAL
G-1	15.0	17.0
G-3	12.5	10.6
G-4	11.5	6.9

DATE OF IRRADIATION
10-11-63 or BEFORE

Figure 23.   Radiation Data for Elements in High-Resistance State.

40
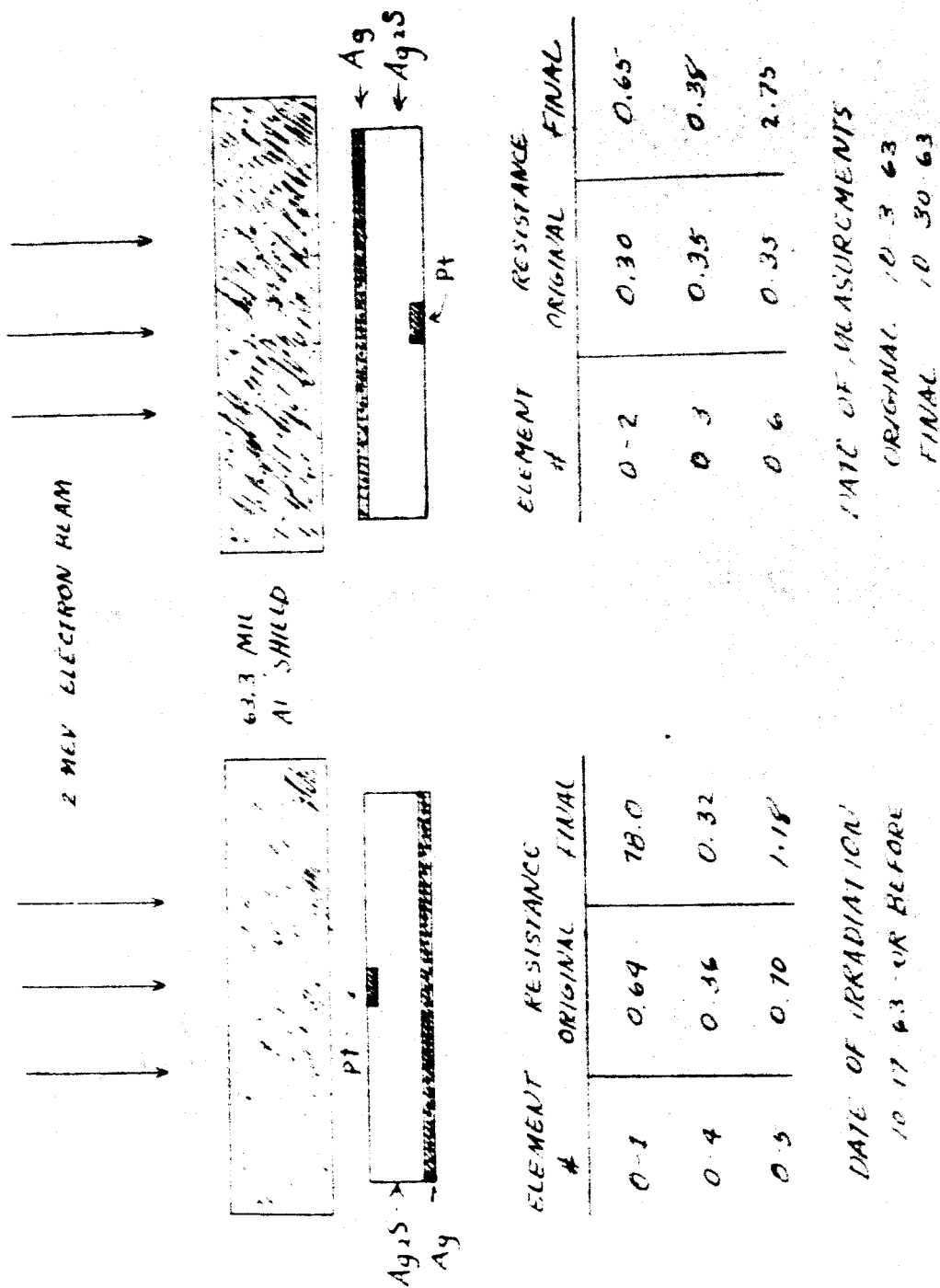
Figure 24. Radiation Data for Elements in Low-Resistance State

believe that the x-rays contributed to the changes observed in the elements. Comparatively, the electrons would be expected to be more effective when the smaller platinum electrode was towards the beam; the x-rays more effective when the larger silver electrode was towards the beam.

Six other silver sulfide memory elements were also sent to Boeing as control elements; these were not irradiated. Table III indicates the stability of these control units. Those in the low resistance state changed slightly, while those in the high resistance state increased substantially; however, none switched.

This test gives a qualitative indication of the probability of survival of information stored in a silver sulfide memory element that is subjected to an intense electron radiation environment. No tests were made to determine the capabilities of operation within such an environment. The lifetime of these memory elements is drastically reduced, however, by merely exposing them passively to the radiation, even with the shielding used.

The results of cycling tests on memory elements that were exposed unshielded to the electron beam are shown in Figures 25 through 31. All have shortened lifetimes and erratic behavior. Rejuvenation of a worn device to a slightly higher resistance ratio by substantially increasing the pulse duration is indicated for element 3, Figure 27, but is not apparent for element 12, Figure 31.

Two memory elements that were shielded by the 63.3 mil thick aluminum sheet during the irradiation performed in the cycling tests as shown in Figures 32 through 35. Their shortened lifetimes and more erratic behavior is evident.

The effects of greatly reduced ambient pressure on the operating characteristics were qualitatively evaluated by a simple experiment.

Figure 25. Initial Cycling Data for Irradiated Element, G-1
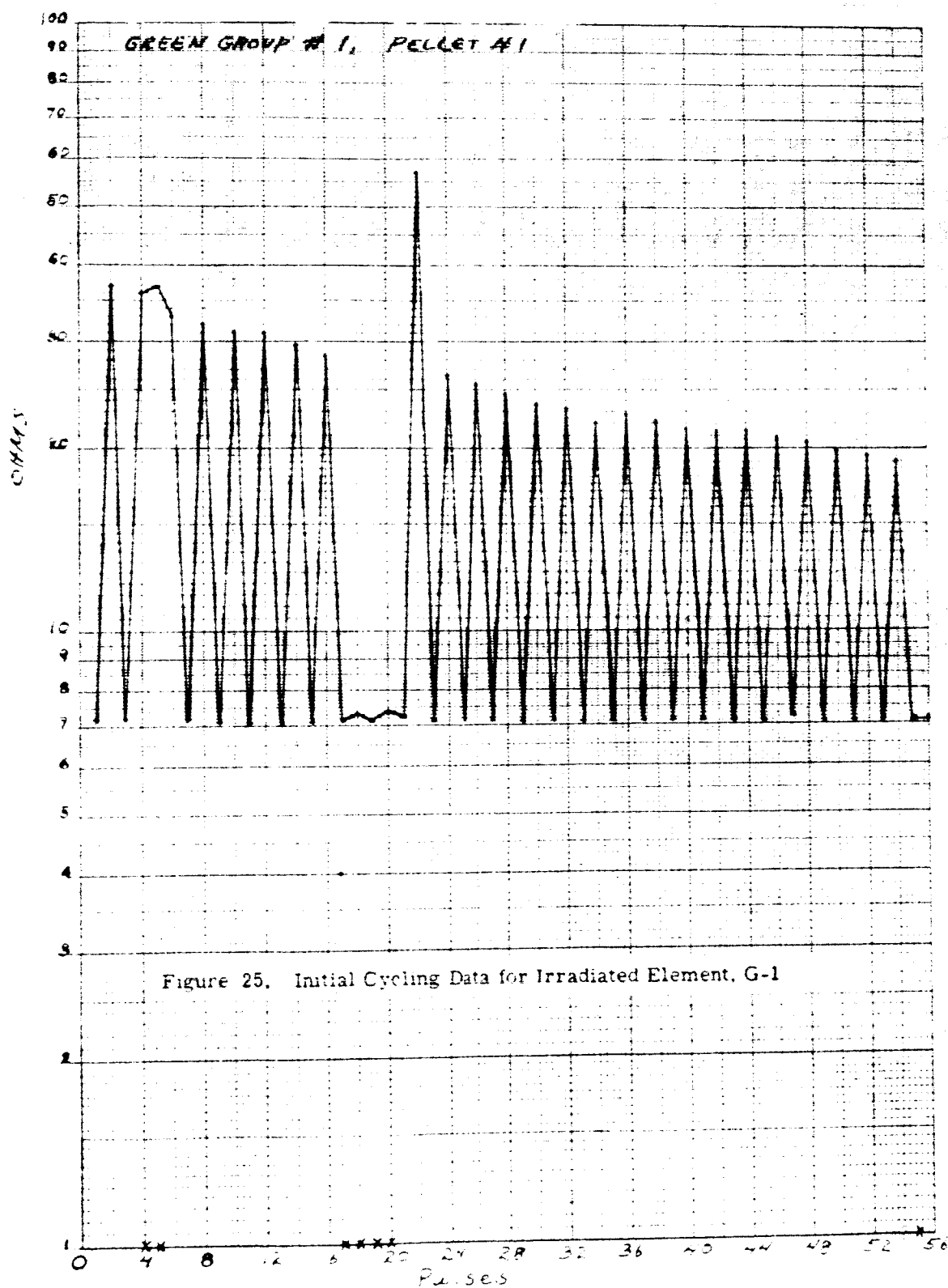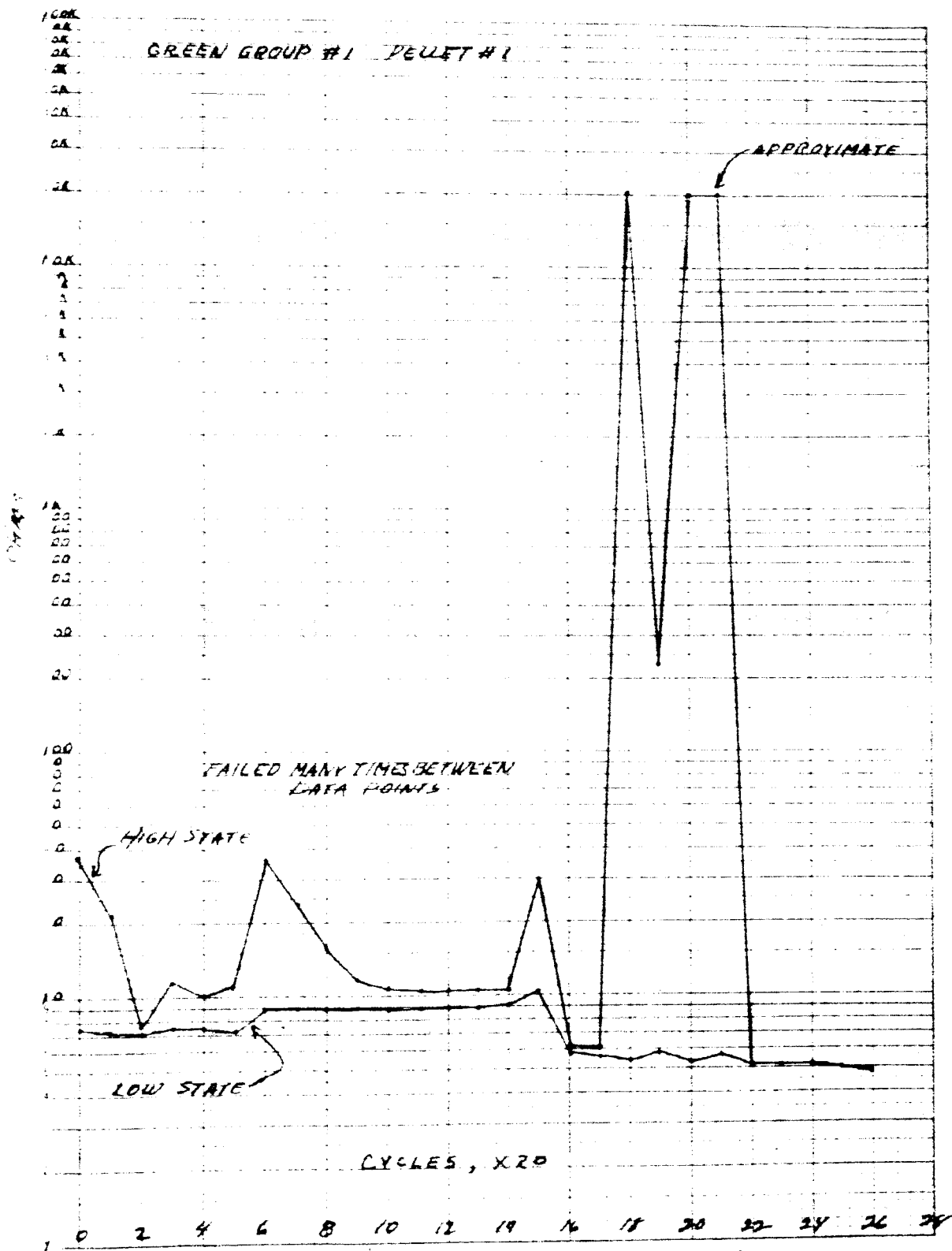
Figure 26. Sampled Cycling Data for Irradiated Element. G-1

44

Figure 27. Sampled Cycling Data for Irradiated Element, G-3

45
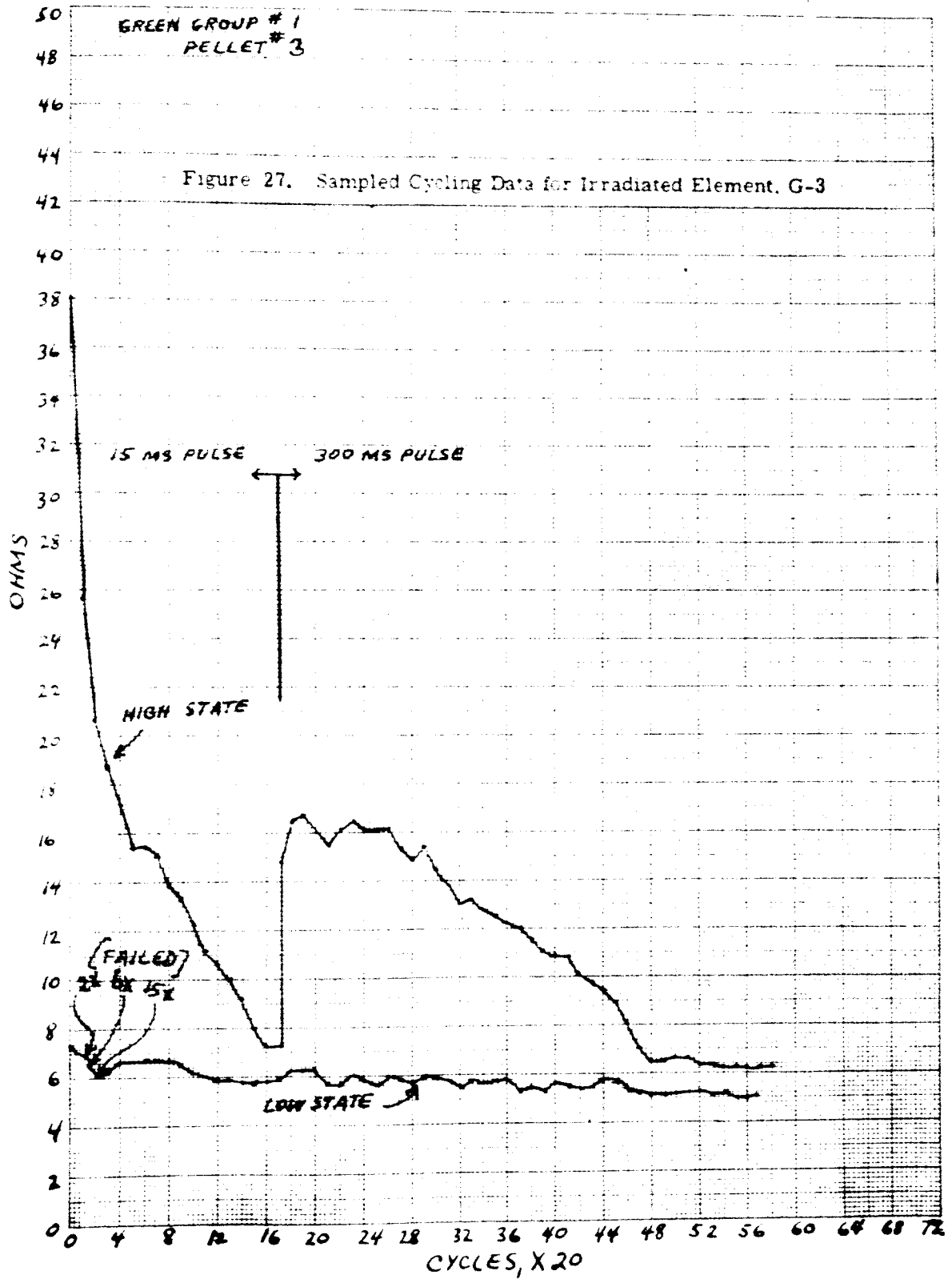
GREEN GROUP #1 PELLET #4

Figure 26. Initial Cycling Data for Irradiated Element, G-4
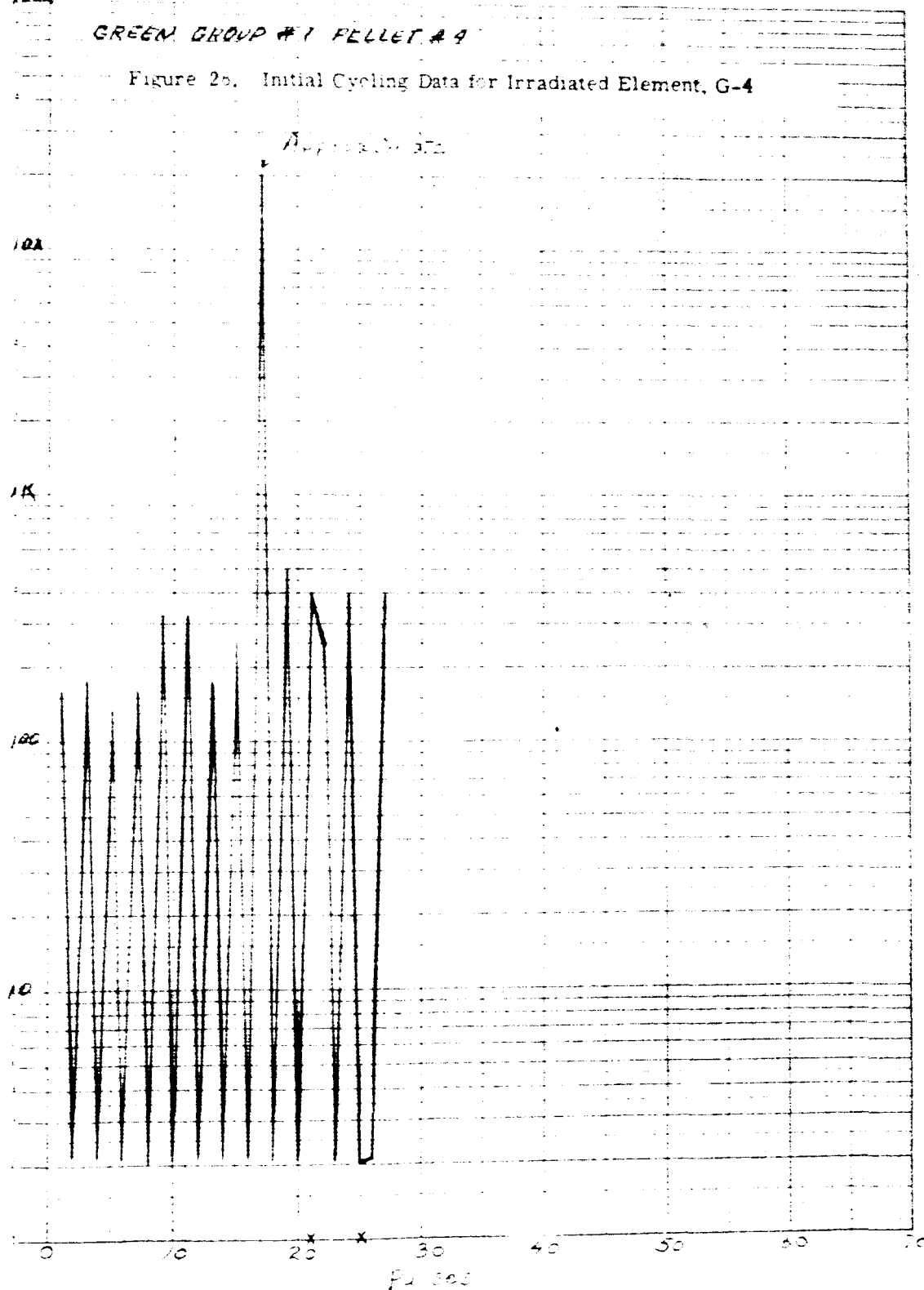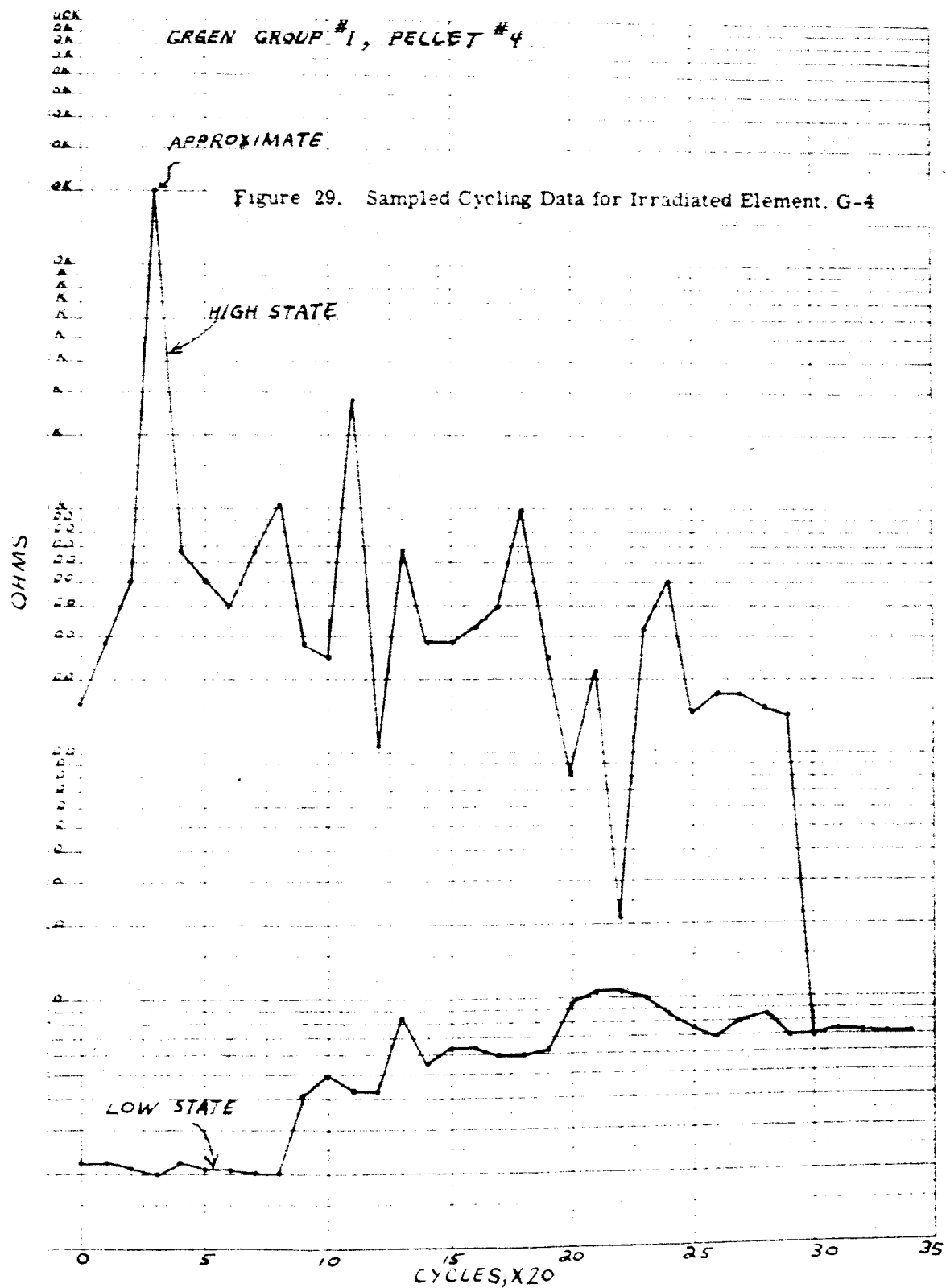
Figure 29. Sampled Cycling Data for Irradiated Element. G-4
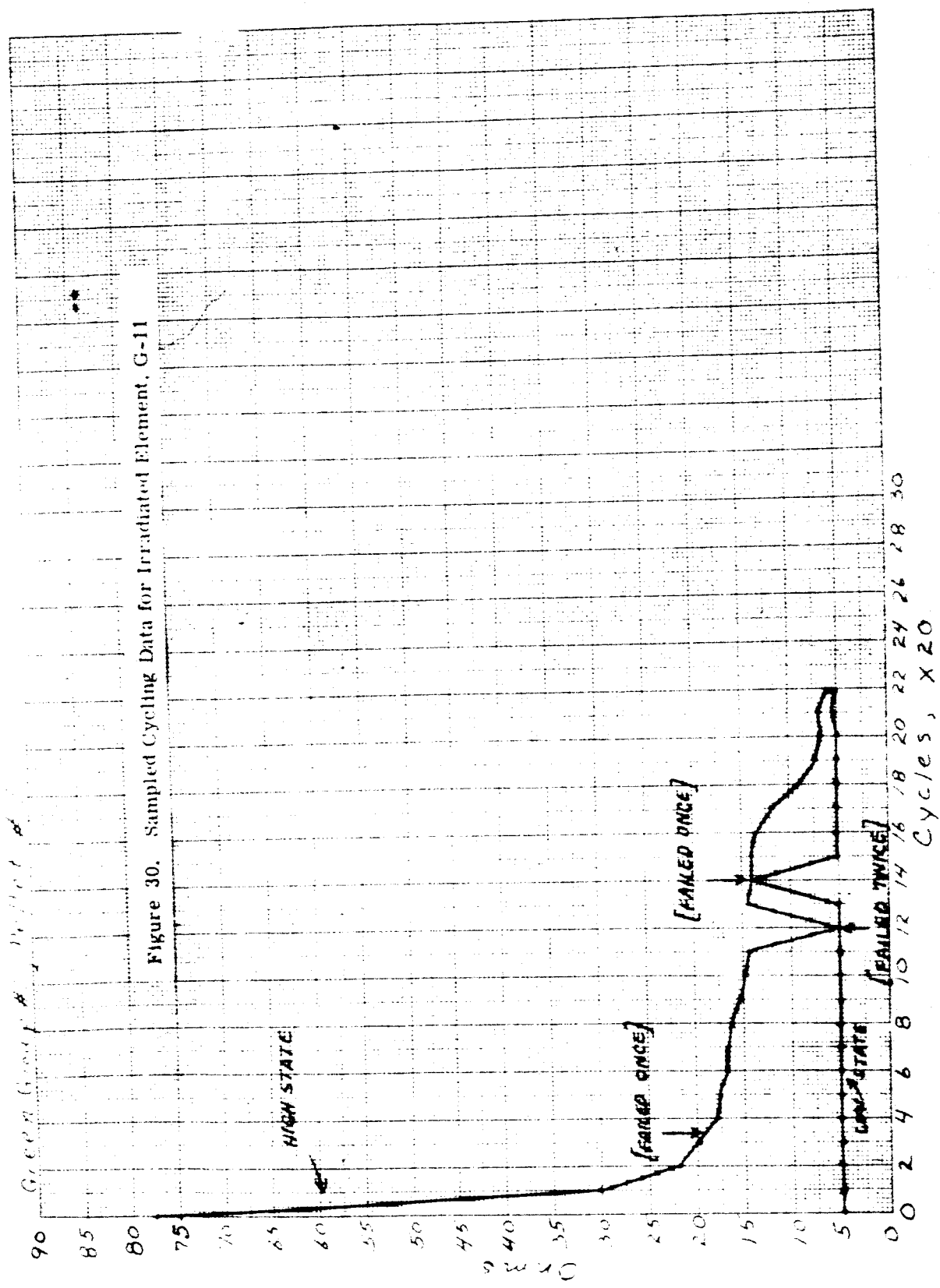
Figure 30. Sampled Cycling Data for Irradiated Element, G-11

48
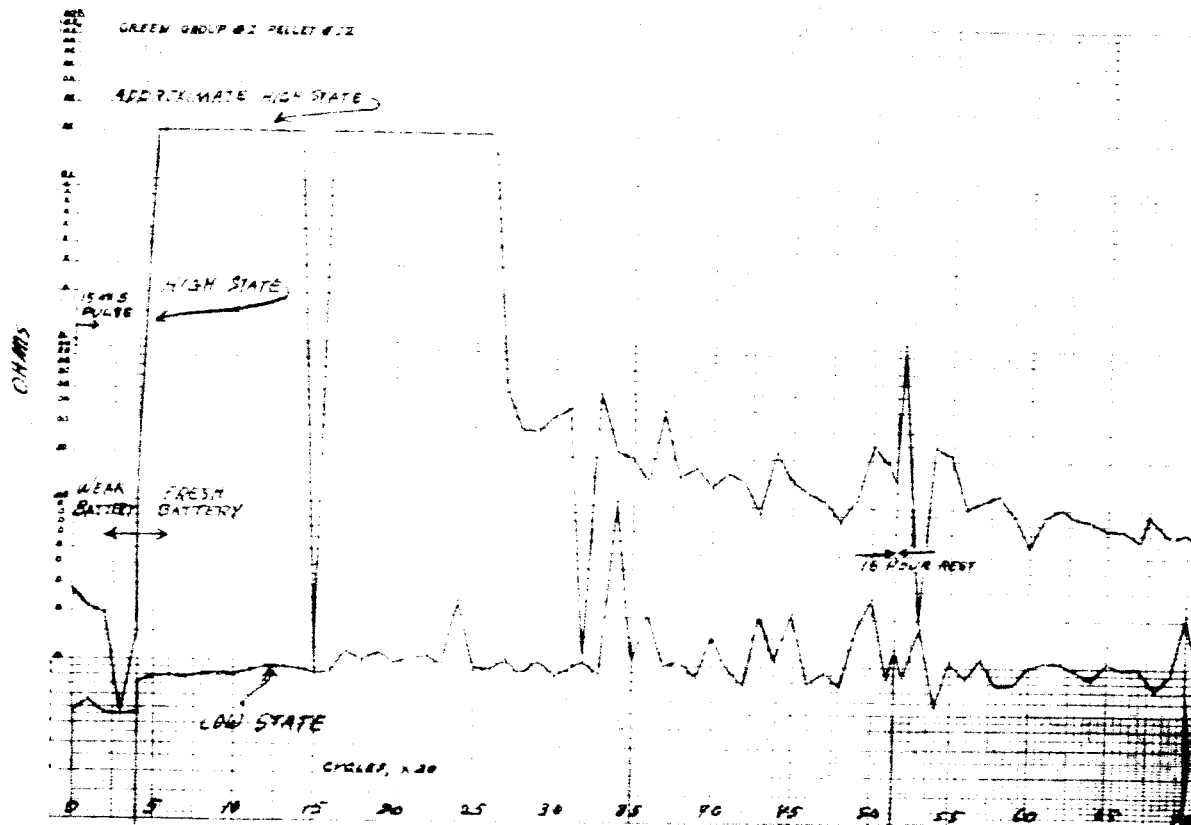
Figure 3.   Sampled Lifetime Data for Irradiated Element G-12
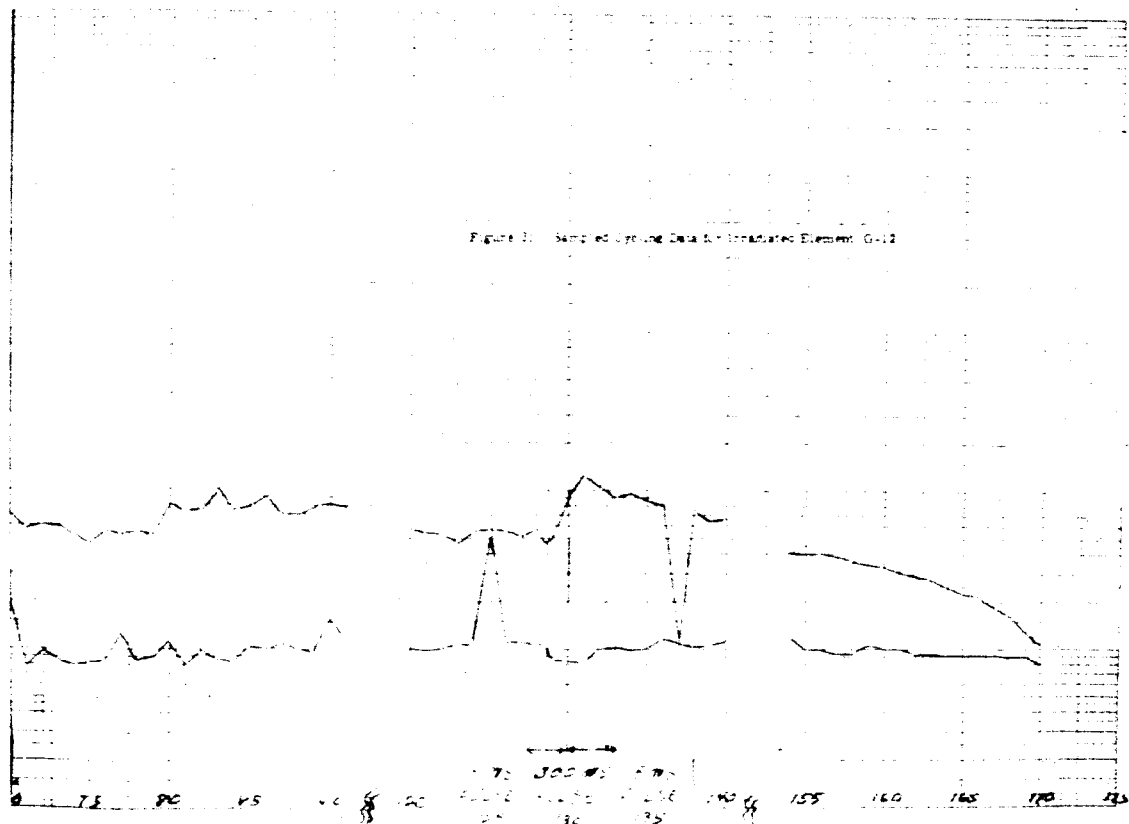
ORANGE GROUP #2   PELLET #2

Figure 32.   Initial Cycling Data for Irradiated Element, 0-2

OHMS

PULSES

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Figure 33. Sampled Cycling Data for Irradiated Element. 0-2

Figure 34. Initial Cycling Data for Irradiated Element, 0-6

Figure 35. Sampled Cycling Data for Irradiated Element, 0-6
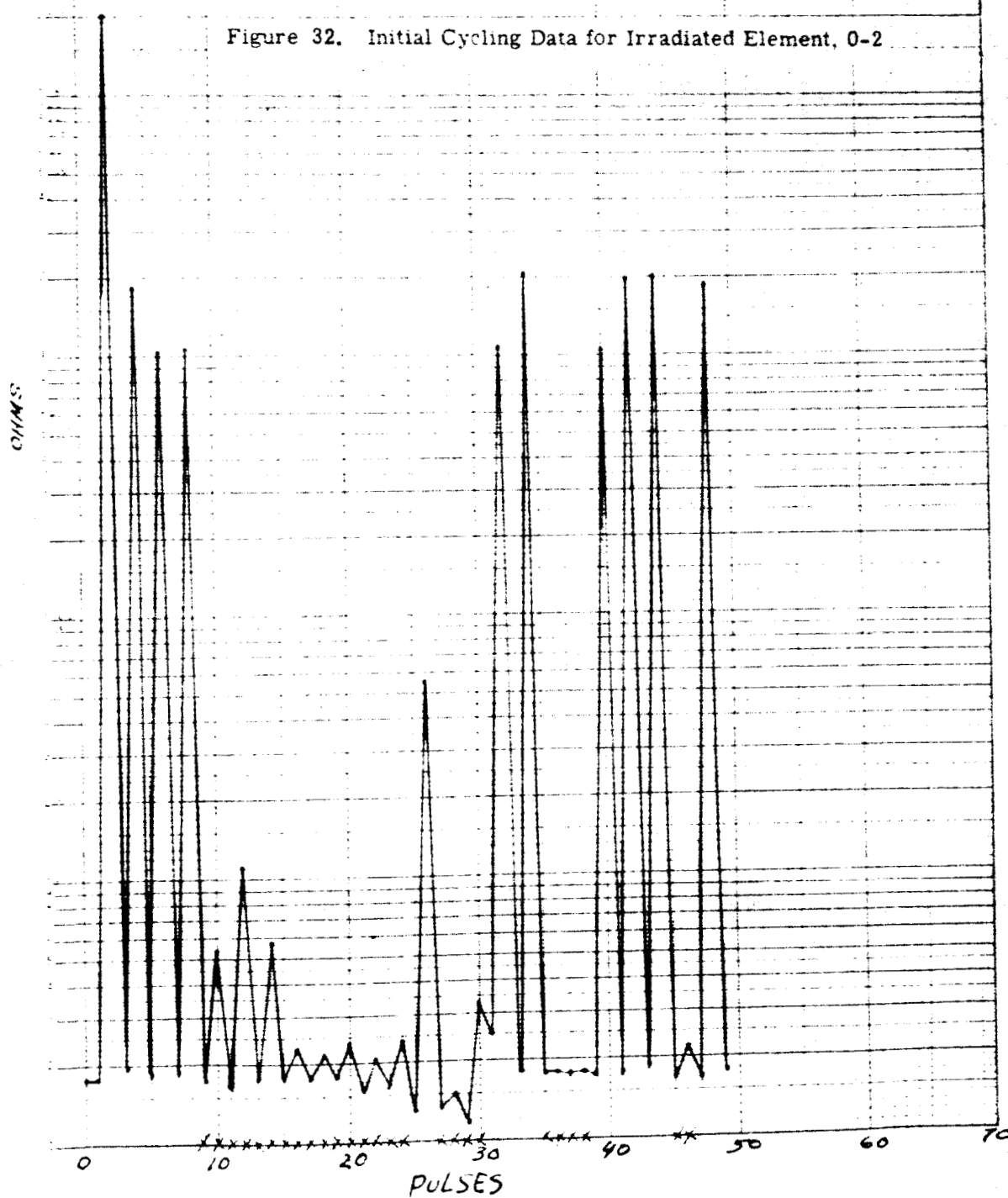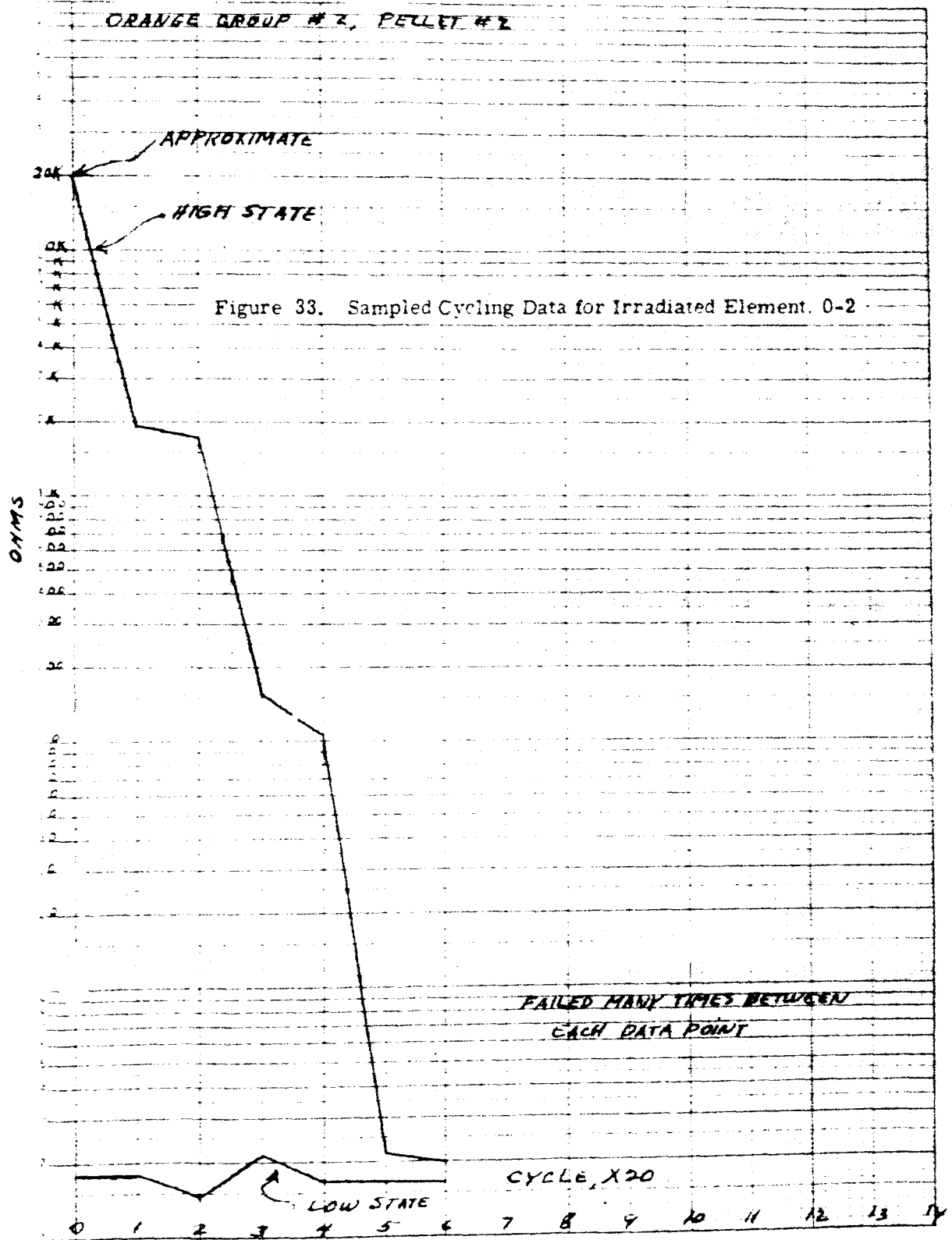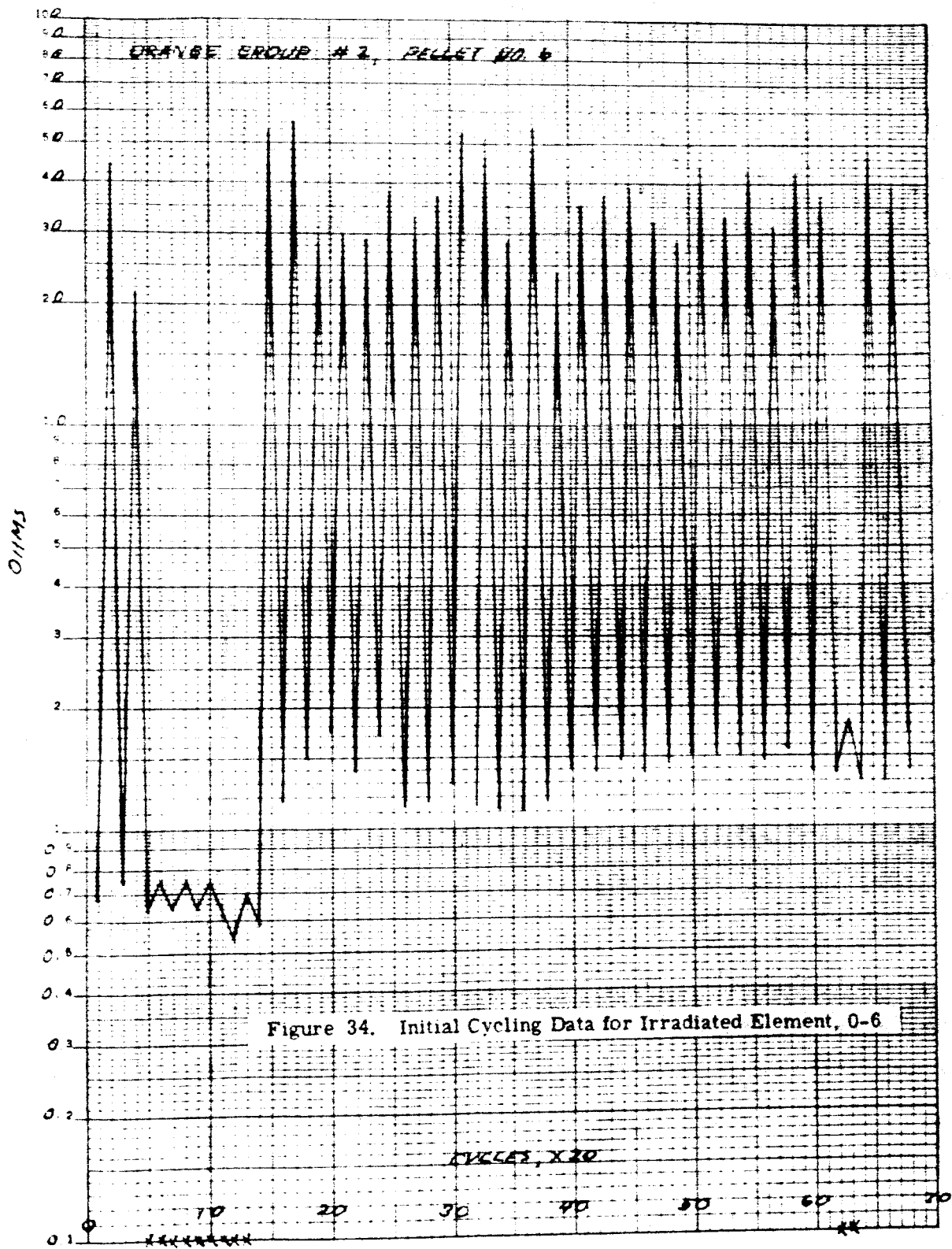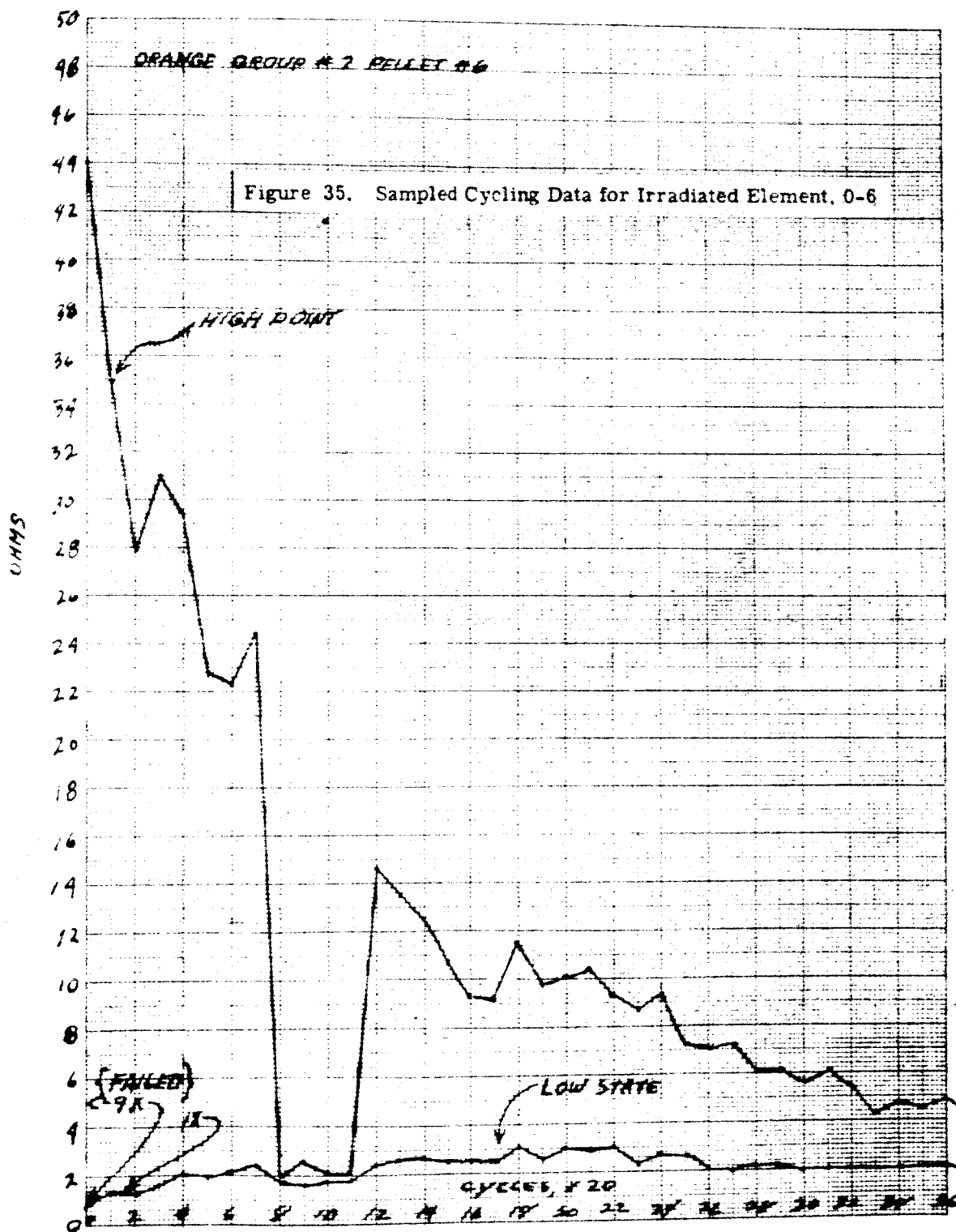
TABLE III

Stability of Control Elements

Low State:

R E S I S T A N C E

Element No.	Original	Final
0 - 11	1.37	2.20
0 - 12	0.43	0.42
0 - 13	0.76	0.66

High State:

R E S I S T A N C E

Element No.	Original	Final
0 - 7	360	550
0 - 8	125	143
0 - 10	100	193

Date of Measurement:

Original	10-3-63
Final	10-30-63

Silver sulfide memory elements were placed in a vessel evacuated to about 1×10^{-2} to 1×10^{-3} torr. While in this environment, the cycling characteristics and storage characteristics were determined. From the oscillograph traces, the elements appeared to operate in the same manner as at atmospheric pressure.

An element was immersed in liquid nitrogen and observed to operate at -196° C.

One element was set in the high state and another in the low state, and their resistance values were determined using a low amplitude, 1 kilocycle a-c signal at various times while in the evacuated chamber. The changes found in both resistance states were of the same order as those changes observed in comparable units stored for a similar period at normal pressure.

Resistance measurements were made in air on memory elements at various temperatures up to 200° C to determine the retention of information. Seven elements were used in this test; elements 1 through 3 were initially in the low state; 4 through 7 in the high state. Resistance measurements were made by the a-c bridge method.

The results of the test are shown in Table IV. The test was stopped at 200° C, and the units were allowed to return to room temperature; the resistance was again measured. The results after returning to room temperature are shown in the last line of Table IV. At 127°, those pellets which were in the low state remained in the low state with resistances not far different from the initial 25° C values; those which were in the high state remained in that state, even though the resistances decreased. On cooling to room temperature, those with the low resistances returned to resistances roughly equal to or higher than the original values. Those in the high state were substantially higher. Thus, information may be read at 125°, and is readable at room temperature after exposure to 200°:

It is to be noted that stored information is not lost when the element passes through the β-α transformation at 179° C.

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TABLE IV

Resistance Versus Temperature

Temp. °C	RESISTANCE IN OHMS						
	----Low State----			---------High State---------			
	1	2	3	4	5	6	7
25°	.46	.67	1.0	2300	72	1000	210
46°	.33	.67	.44	2800	58	1100	226
66°	.34	.67	.44	2200	50	770	165
98°	.38	.69	.42	900	40	405	106
127°	.46	.73	.42	280	20.5	198	68
150°	.59	.79	.43	69	12.2	64	28
180°	.61	.77	.48	23	5.2	24	10.2
200°	.58	.54	.52	9.0	1.96	8.8	5.0
25°	.6	1.37	1.08	4300	142	2000	3400

Silver sulfide memory elements were stored at a laboratory temperature and pressure to evaluate the retention of information. Two short-term storage tests were made; one for 16 hours and one for 72 hours. The results are shown in Table V. Although some of the measured resistance values changed slightly, none of the elements appeared to switch spontaneously.

TABLE V

Short-Term Storage

Element	RESISTANCE, OHMS Initial	RESISTANCE, OHMS 16 Hours Later	Element	RESISTANCE, OHMS Initial	RESISTANCE, OHMS 72 Hours Later
1	2.3 K	2.55 K	11	2.45 K	2.85 K
2	72	44.3	12	180	175
3	1.0 K	1.06 K	13	820	890
4	210	220	14	4 K	3.85 K
5	325	360	15	0.62	0.79
6	6.9	7.5	16	0.4	0.45
7	0.36	0.46	17	67.5	390
8	0.65	0.67	18	0.57	0.7
9	0.9	1.0			
10	0.63	0.60			

The same general results were obtained from elements stored for eight months, Table VI. In the long-term storage test, the initial resistance measurements were made on April 5, 1963, with d-c ohmmeter. The resistances changed during this measurement. In the two subsequent measurements, August 21, 1963, and January 5, 1964, the resistances were measured on a 1-kilocycle low-level a-c bridge.

TABLE VI

Long-Term Storage

RESISTANCE IN OHMS

Element	5 Apr. 1963*	21 Aug. 1963	5 Jan. 1964
1	10 K	750	870
2	6 K	620	1.1 K
3	6 K	1.34 K	5-10 M (Erratic)
4	0.5	1.1	1.73
5	0.8	0.8	0.87

*These measurements were made with a d-c ohmmeter; the others were made with an a-c bridge.

An increased frequency can also be used for reading with the a-c bridge, provided the signal level is low enough to keep the memory element from switching, as shown in Table VII. When the signal level is maintained constant, as was done in this test, no significant changes in the impedance are found over the 1 to 10 kilocycle range.

TABLE VII

High-State Resistance vs Frequency of Measurement

Element	RESISTANCE IN OHMS		
	1 kc	5 kc	10 kc
1	25.0	25.0	24.5
2	36.2	37.0	37.0
3	9.3	9.4	9.3
4	7.8	7.8	7.8
5	48.0	49.3	49.6
6	6.4	6.3	6.3
7	9.8	9.8	9.7
8	5.8	5.8	5.8
9	6.3	6.2	6.2
10	38.5	38.0	38.2

SWITCHING PATH

A study of the potential distribution in an unused silver sulfide element using the standard two-dimensional resistance paper-and-voltage probe technique for field mapping was made on units having the approximate dimensions of Figure 36. The results for two electrode configurations are shown in Figures 37 and 38. It should be noted that nearly the entire potential distribution on the silver sulfide surface occurs very close to the small electrode; thus, the field intensity is concentrated in these small circular or annular areas. Such a distribution of potential gradient can be correlated with the particle motion observed microscopically, as will be described shortly. This initial potential configuration will change when the switching cycle commences and will undoubtedly continue to change throughout the entire operating life of the memory element. Although the average field strength directly between the electrodes is relatively small, it is obvious that much higher fields will predominate near the edges and corners of the smaller

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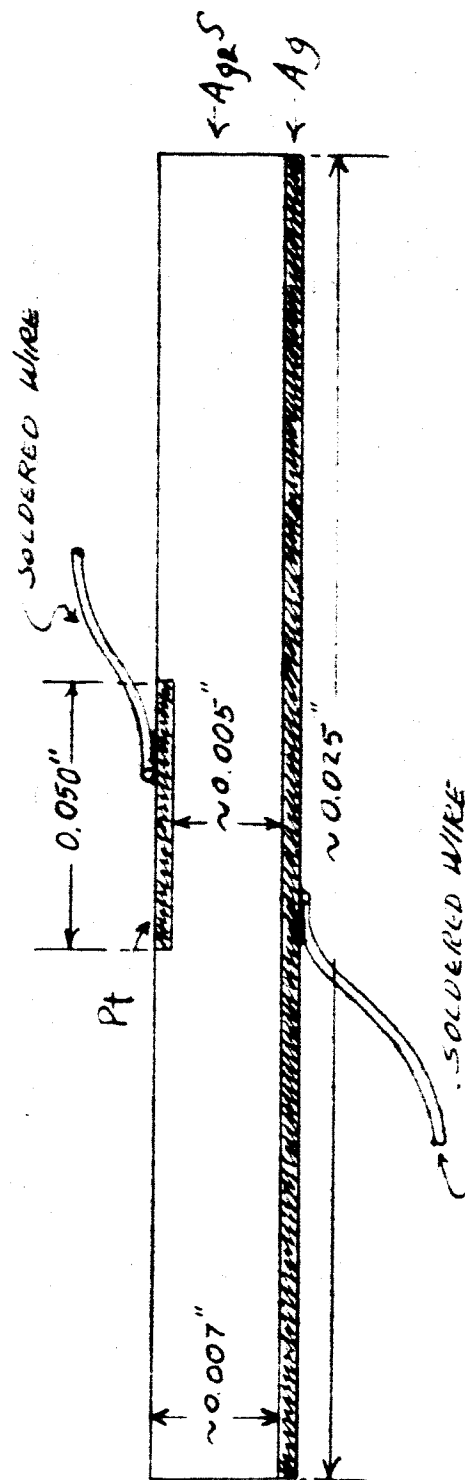
Figure 36. Approximate Dimensions of Typical Test Element

PENETRATION OF POINT = 0.001"
ELEMENT THICKNESS = 0.007"

TWO-DIMENSIONAL CROSS SECTION.
AXIS OF MEMORY ELEMENT

$V = V_0$
$V = \frac{5}{6} V_0$
$V = \frac{4}{6} V_0$
$V = \frac{3}{6} V_0$
$V = \frac{2}{6} V_0$
$V = \frac{1}{6} V_0$
$V = 0$
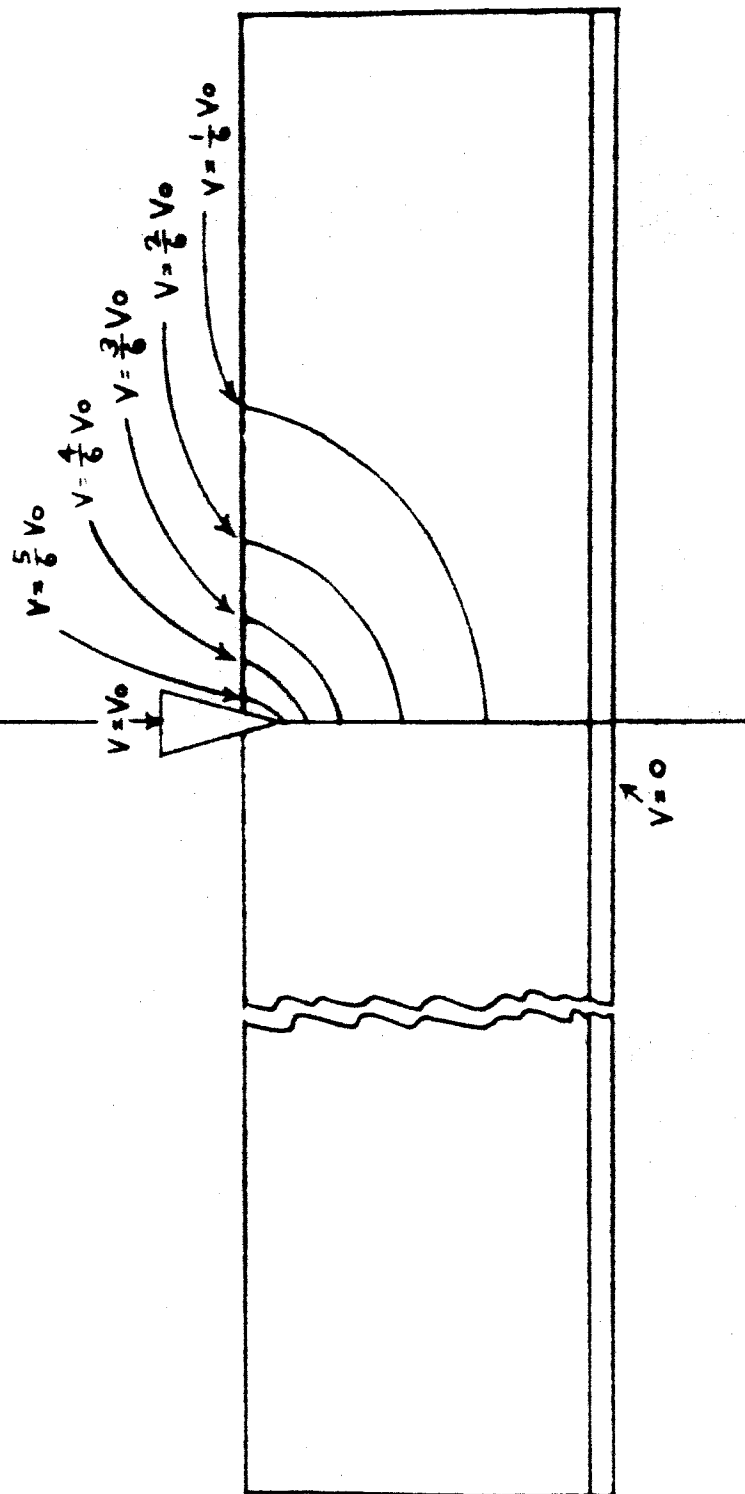
Figure 37.   Potential Distribution in Unformed Element

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TWO-DIMENSIONAL CROSS SECTION

TYPICAL PRESSED ELECTRODES

AXIS OF MEMORY ELEMENT

$V = \frac{4}{5} V_0$

$V = \frac{3}{5} V_0$

$V = \frac{2}{5} V_0$

$V = \frac{1}{5} V_0$

$V = 0$

$V = V_0$

r (LARGE ELECTRODE) $= 0.106''$

r (SMALL ELECTRODE) $= 0.020''$

THICKNESS SMALL ELECTRODE $= 0.002''$

THICKNESS Ag₂S $= 0.007''$
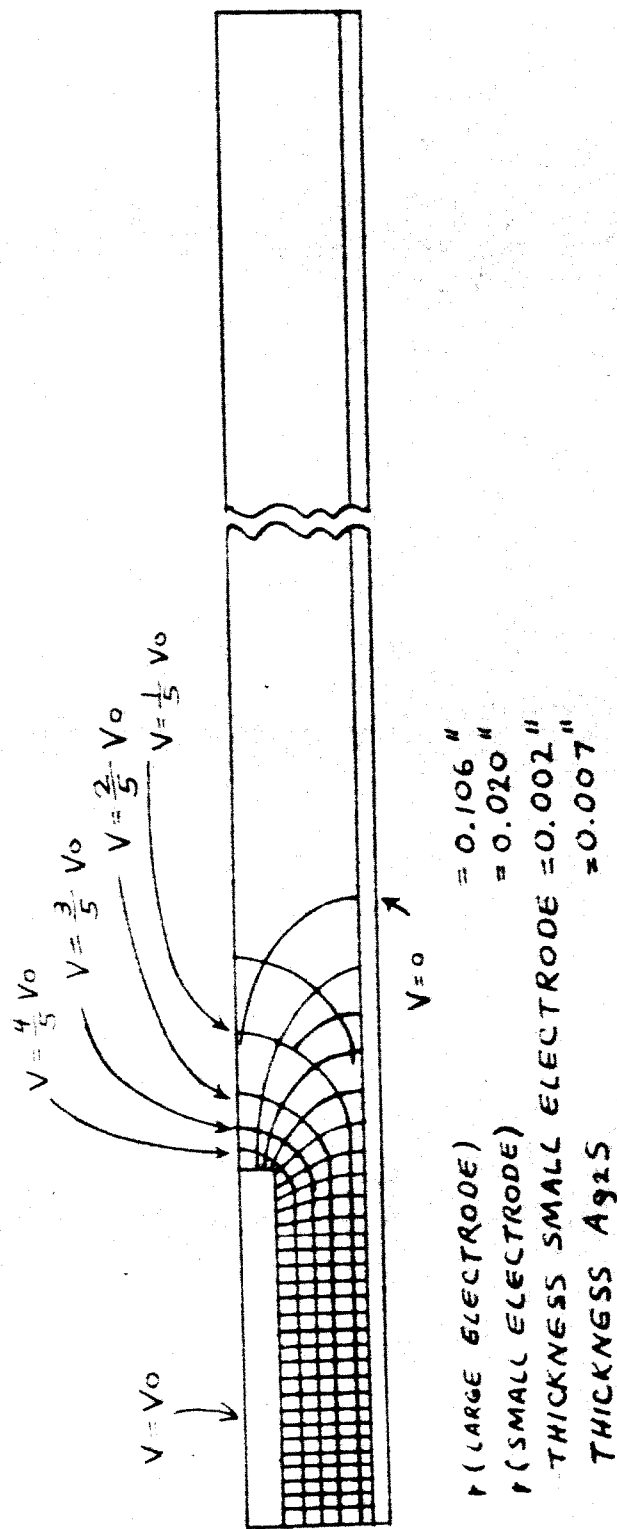
Figure 38. Potential Distribution in Unformed Element

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electrode. The role of these fields in the forming and switching processes is unknown.

A microscopic observation of the silver sulfide units was made at 60 to 120 X during both the forming process and the switching between the two stable resistance states. Initially, a tungsten needle was used as one electrode. It was soon found that the needle, if resting on the surface of the silver sulfide by gravity, would burrow its way through the wafer to the silver electrode. This, besides showing evidence of melting in the switching path, also indicated that the α or high-temperature phase of silver sulfide, stable above 179° C, was formed during some part of the switching process.

When the tip of the tungsten needle was moved from the axis and mounted rigidly on or very near to the periphery, the actual forming process was observed on the exposed vertical surface of the element. During the part of the forming operation preceding the true breakdown, much silver, seemingly in the form of minute balls, came to the flat surface in a large area surrounding the needle and also on the vertical surface. This, of course, is with the negative 2 volts applied to the needle. During forming, a wide path of silver between the electrodes was formed. This apparently takes a least resistance rather than a direct path.

Furthermore, the concentration of silver was very great and spread laterally along the silver - silver sulfide interface. The area midway between the extremities of this switching path seemed somewhat deficient in silver relative to the other areas. The pre-forming plating of silver and the varying silver concentrations in the switching path might possibly be attributed to the dependence of the diffusion of the free silver on temperature. Another investigator[6] has observed that the free silver diffuses into the colder areas of the silver sulfide; hence, the silver paths would be orthogonal to the equithermal lines between the electrodes and thus be plated over a wide area on the surface, concentric with the small circular electrode. Also, the electrodes would act as effective heat sinks and could therefore cause concentration variations in the switching path.

Additional motion of silver between the electrodes was observed
during the switching process. This appeared like ripples or waves;
the direction depended upon the polarity of the applied potential.
This visible motion of silver initially occurred over the entire path
although concentrated more in the middle. As the unit was cycled
further, the silver migration gradually became entirely concentrated
adjacent to the tungsten needle. Some melting was also observed there.
At the same time, the delay in switching from the low to high state
became much longer. When all apparent silver motion ceased, the memory
element also failed to switch.

More microscopic observations were made on a wafer having an impressed
circular platinum electrode similar to Figure 36. Again, during the form-
ing stage, plating of silver over much of the surface was observed. Be-
cause of this type of construction, the actual switching path could not be
seen. However, as the unit switched states, a motion of silver on the
surface near the exposed platinum - silver sulfide interface was clearly
apparent. The momentary directions corresponded to the polarity of the
applied potential. Initially, this motion was seen around the entire
periphery of the platinum electrode and extending into the silver sulfide.
As cycling continued, this action eventually became localized at only a
few points. As with the previous example, the delay time in switching
again was longer. That the motion of particles observed was radial with
and close to the small platinum electrode is not too surprising since the
majority of the electric field is concentrated in this region.

Several silver sulfide memory elements were examined by sectioning
and by dissolving the silver sulfide with a thiourea-hydrochloric acid
solution. This acid dissolves silver sulfide at a moderate rate and
attacks silver and the electrode metals at a very slow rate. Some of the
samples which have been cycled to failure have shown a fine network of
silver in the silver sulfide, the amount of silver being greatest in the
silver sulfide near the platinum electrode.

Another experiment revealed that a photovoltage was generated when an unformed silver sulfide element was exposed to an approximately 250-microsecond duration unfiltered flash from an FX-1 xenon tube. Electrical screening and optical masking variations indicated that this voltage was generated only at the platinum electrode - silver sulfide interface or surface junction. Potentials up to 40 millivolts could be generated depending on the particular element tested. Formed and cycled units did not exhibit this characteristic; thus, there is some evidence that a change in the platinum - silver sulfide interface is necessary for operation of the memory device.

SUMMARY OF OPERATING CHACTERISTICS

The operating characteristics of the silver sulfide memory elements depend on electrical factors such as voltage, pulse duration, and polarity. These factors are interrelated in that they determine the resistance ratios and repeatability, along with other characteristics. The operating characteristics, insofar as they have been determined for elements in the present state of development, are summarized in the following.

Operating voltages in the range of 2 to 12 volts are desirable in order to obtain adequate resistance ratios, although any voltage greater than 0.2 volt may switch the element. The ratio of the resistance in the high state to that in the low state increases as the operating voltage is raised.

Pulses of 15 milliseconds duration were adequate to provide the necessary energy for switching in the voltage range used.

The current required to switch ranges from tens of milliamperes when in the high resistance state to approximately an ampere when in the low state.

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Energy of the order of magnitude of 10^{-4} watt/sec is required to give a resistance ratio of 3. Increasing the energy to approximately 1 watt-sec gives resistance ratios of two orders of magnitude greater. Some of this energy is expended in switching; some of it in heating the element.

There is no switching delay in the sense that switching always occurs during the pulse, although not necessarily in the leading edge of the pulse.

The polarities of the electrodes determine the switching direction. A positive potential on the platinum electrode is required to switch from the low to the high resistance state; a negative potential, from the high to the low resistance state.

Life times as high as 300,000 cycles have been obtained, with resistance ratios near 10. For higher ratios, life times decrease in some inverse manner with respect to the ratio. Failures to switch are randomly distributed throughout the life time, and may amount to about 5% or more of the cycles.

For reading, a 2-volt peak, 100-kilocycle half-wave, sinusoidal voltage is satisfactory. A single pulse of 50 microseconds duration can also be used, provided the rise time is slow. A positive polarity with respect to the platinum electrode is required for reading.

Stored information appears to survive the specific electron bombardment test made, but the operation was not satisfactory since the element failed rapidly.

The memory element operates at -196° C, and also at elevated temperatures with reduced energies. Stored information survives exposure to 125° C.

CHAPTER III. FUTURE WORK

Among the objectives sought in this study, those of the voltages, current, read-out signals, and minimum power, satisfactory for satellite operation, have been attained with the silver sulfide memory element. Other objectives, such as reliability and repeatability have not yet been fully realized. Other factors need to be evaluated more thoroughly, such as improvements which may be obtained with other methods of fabrication, and the effects of space environment. Future work in continuation of this study should be directed along two lines: on one hand, towards improvement of reliability, especially with regard to repeatability in switching, through testing other methods of fabrication of the elements, and on the other hand, towards further evaluation of the characteristics of the elements with respect to operation in space environment.

The technique for making the platinum electrode from powders developed in the last stages of the study, gave an indication, in what little testing could be done on elements with the platinum electrode formed in this way, of a better performance. This should be pursued, as should be other methods of making connections. Other modifications deserve study; these include a reduction of the volume and changes of the conductivity of silver sulfide. These modifications of the method of fabrication should be studied and evaluated in terms of reliability of switching. A bi-product of this phase would be progress towards better understanding of the mechanism of switching.

The study and evaluation of the characteristics of the silver sulfide memory elements should be refined and continued in the direction of extending the determination of the frequency of failure to switch and reducing it, as well as in the direction of increasing the lifetime in cycling. The method of recording these factors automatically, established in the latter stages of this study, would be used in future work along with computer methods of evaluating the data. Attempts should be made to measure the energy required for switching. Tests of the effects of pressure

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and temperature, to simulate the space environment, need to be widened. Ultimately, tests of operation of a memory plane assembled from silver sulfide memory elements appears to be desirable. At such a time as it can be shown that an array of these elements can operate reliably, it would then be desirable to establish a research and development program for producing the silver sulfide memory elements reliably and economically.

CHAPTER IV. CONCLUSIONS AND RECOMMENDATIONS

This study of silver sulfide as a memory element having two stable resistance states, while not yet complete, has led to the conclusions which follow.

Silver sulfide is a bistable resistive material which is switchable between two resistance states with 15 millisecond pulses of low energies at low voltages. Ratios between 3 and 100 or more, for the resistance in the high state to the resistance in the low state, are obtainable, depending on the applied voltage. Resistances may be read nondestructively with 50 microsecond pulses of 2 volts. Information stored in such elements does not deteriorate during storage for several months, nor is it lost on exposure to over $125^{\circ}C$, or to high energy electron beams. Such elements are operable at $-196^{\circ}C$, as well as in vacuum. All of these characteristics are favorable for space applications.

There are two other characteristics which, insofar as they have been studied, are less favorable for those applications. The life time of the element observed in cycling, about 3×10^5 sycles, implies limited serviceability. The rate of failure to switch, about 5%, implies the need for improving reliability. However, there are indications that improvements may be obtained by modification of the design of the element, as well as the method of fabricating it.

On the basis of these conclusions, it is recommended that this study be continued in the two directions of improvement of life-time and reliability by testing changes in design and methods of fabrication, and of the evaluation of the element with respect to operation in the space environment.

CHAPTER V. NEW TECHNOLOGY

One item of new technology was developed during the period of this study, namely a method of fabricating a resistive memory element from powdered materials.

The preferred procedure for making silver sulfide memory elements with the electrodes attached to the resistive pellet is as follows:

(1) Place in the cavity of a 0.25-inch die sufficient silver powder to cover the bottom, press lightly into position by rotating and tapping the plunger;

(2) add 55 mg of 100 - 200 mesh silver sulfide from a plastic dispenser, press into position as described above;

(3) add about 1 mg of minus 200 mesh platinum powder by means of a plastic dispenser, using a special aluminum funnel to confine the platinum to a 0.05-inch diameter spot at the center of the pellet, press lightly; then

(4) complete fabrication of the pellet in a hydraulic press, using 140,000 pounds per square inch.

The thickness of the silver sulfide pellets so prepared is nominally 0.007 inch. Elements formed in this way are sufficiently sturdy to permit any reasonable handling without breakage.

The operating characteristics of silver sulfide memory elements fabricated by this procedure are given in the section of this report "SUMMARY OF OPERATING CHARACTERISTICS", pages 64 and 65. .

The development of a procedure for fabricating a bistable resistive memory element is one of the objectives of this study.

While the technology described here was developed primarily for fabricating a bistable resistive memory element, it may be used for fabricating other electrical devices consisting of two electrodes separated by solid materials having any desired characteristics.

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RESISTANCE OF TRUNCATED CODE

$$r = r - mz$$

$$m = \frac{r}{L}$$
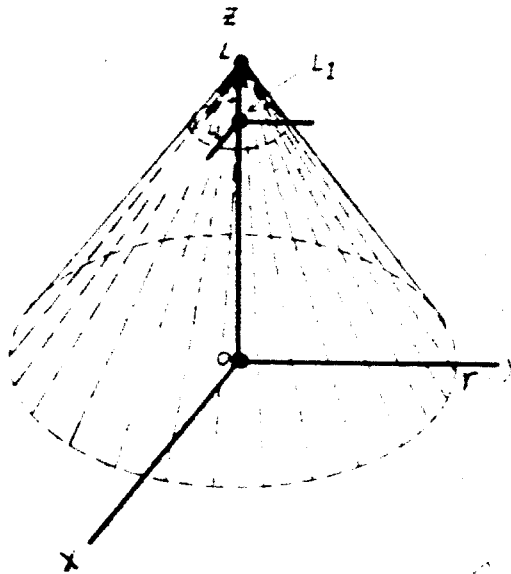
$$R_{TC} = \rho \cdot \frac{\ell}{A}$$

$$= \rho \int_{0}^{L_1} \frac{dz}{\pi (r - mz)^2}$$

$$= \frac{\rho L}{\pi r^2} \left(\frac{L}{L - L_1} - 1 \right) \quad OHMS$$

$$\lim_{L \to \infty} R_{TC} (\text{TRUNCATED CONE}) = R_{R_C} (\text{RIGHT}$$
$$(\text{ie EQUAL AREA ELECTRODE}) \quad \text{CIRCULAR} \atop \text{CYLINDER})$$

L_1 - DISTANCE BETWEEN ELECTRODES

$L - L_1$ - DETERMINED BY RADIUS OF SMALL ELECTRODE
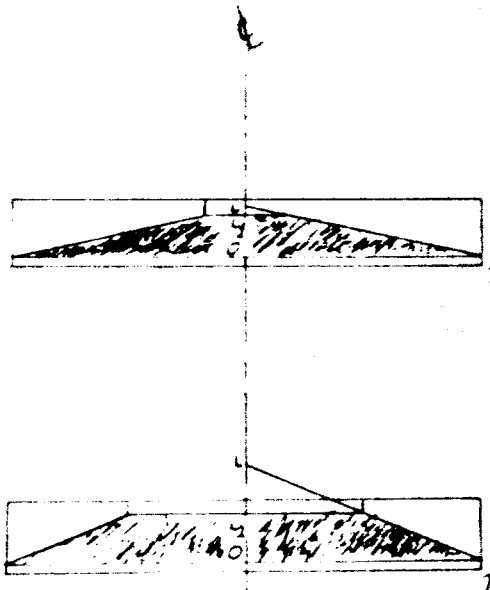
TWO DIMENSIONEL CROSS SECTION

APPENDIX II. ELECTRON IRRADIATION

THE BOEING COMPANY
AERO-SPACE DIVISION
Seattle, Washington

FINAL REPORT

ELECTRON IRRADIATION

I. Items Received

The following groups of Ag_2S devices were received for electron irradiation:

Green Group V; six devices for setup procedures

Green Group I; six devices to be irradiated

Orange Group II; six devices to be irradiated

Control Group III; not to be opened nor irradiated

Control Group IV; not to be opened nor irradiated

II. Irradiation Requirements

1. Integrated does 3 x 10^{-8} amp-hr/cm^2

2. Beam current to be such as to not cause the device temperature to exceed 150°C.

3. Beam energy greater than 0.5 Mev.

4. One group of six to be irradiated in the direct beam. Other group of six to be irradiated through an aluminum shield of between 300 to 600 mg/cm^2.

5. In each group of six devices, three must have their Ag coated side toward the incident beam and three must have the Ag_2S side containing the Pt spot toward the incident beam.

III. Test Information

All devices in Green Group I and Orange Group II were irradiated at the same time. This was accomplished by scanning the output electron beam over a 24" path, measured at the scan window (.005" titanium). The devices were located 3" from the scan window, along the beam path, and as close to the zero scan position of the beam as possible.

The following steps in the irradiation were performed:

1. A low mass, non-metallic, device holder was constructed to hold the devices. The holder was located approximately 1" away, parallel to the beam scan path.

2. A PVC scan picture was made to locate the exact beam trace with respect to the holder. The PVC scan is enclosed.

3. A small Faraday cup having an entrance opening of 1 cm^2 was mounted at the center of the scan on the device holder, and the output of the Faraday cup run into an El Dorado Model CI 110 current integrator. A test run was made to establish the correlation between machine current, Faraday cup current and irradiation time. A machine current of 45 μa yielded a target current of .143 μa and an irradiation time of approximately 800 seconds.

4. In order to establish the temperature rise of a device during irradiation one of the devices from Green Group V was equipped with a Fenwall Thermistor type GB43J1 and calibrated over a range of 0° to 150° C. This device was run along with the Faraday cup to the parameters established in step 3. Prior to irradiation the device temperature was 24° C. During irradiation the device temperature rose to 26° C. Because of the small temperature rise indicated in this test, no attempt was made to measure the temperature rise of Green Group I or Orange Group II during irradiation.

II-2

This one device from Green Group V is the only device used from this group. The remaining five in the package have not been irradiated. We enclose the one device used with the thermistor mounted on it, as well as the unirradiated ones.

5. A cross calibration was made between the Faraday cup and fluorescent degradation in cobalt glass chips. During a one second calibration run at 45 μa beam current the cobalt glass yielded a dose figure of 36.8 ±5.0 kr (Co^{60} equivalent) which corresponds to a 2 Mev electron current of .147 ±.02 μa/cm^2. This compares favorably with the Faraday cup corrected current of .128 μa.

6. Finally all devices in Green Group I and Orange Group IV were irradiated in one run as follows:

(a) Green Group I was run in the direct beam with devices #1, 3, 4 having the Ag plated side away from the incident beam and #10, 11, 12 with the Ag plated side toward the incident beam. These devices were placed in a line on one side of the Faraday cup.

Orange Group IV was exposed under a piece of aluminum having a thickness of 63.3 mils (we are including the aluminum slab used), with devices #1, 4, 5 having the Ag plated side away from the incident beam and devices #2, 3, 6 with the Ag plated side toward the incident beam. These devices were placed in a line on the opposite side of the Faraday cup from Green Group I.

When we opened the Orange Group IV package the numbers 4 and 5 had come off two of the devices. Also number 1 was so loosely attached that we are not sure that it may not have transferred in the package. We placed the numbers 4 and 5 back on arbitrarily. We hope you can

resolve which ones are actually 1, 4 and 5. We refastened all the numbers since most of them did not look like they would stick on much longer.

(b) The total integrated electron dose to these devices was 3.0×10^{-9} (+10%, -5%) amp-hrs/cm^2. This equates to a dose of 2.8×10^7r (Co^{60} equivalent).

(c) The time required for irradiation was 834 seconds.

(d) The average irradiation rate was 0.13 μa/cm^2.

(e) The temperature rise was negligible--not over several degrees.

(f) The incident electron energy spectrum was 2 Mev ± 0.3%.

APPENDIX III. SILVER SULFIDE COMPARED WITH ANTIMONY TRISULFIDE AND NICKEL OXIDE

In addition to silver sulfide, two substances have been studied and tested for their switching properties. In an investigation of the electrical and optical properties of antimony trisulfide, Davis[11] discovered that, when this substance contains excess antimony, a low resistance path is formed by a field of the order of 10^3 volts/cm. The switching effect in this nonstoichiometric substance was studied by Gildart et al[12] who directed their attention mainly to the breakdown between two electrodes attached to a common plane surface of the cast sulfide. The UNIVAC Research Division made a brief test of some of the switching characteristics between opposite surfaces of nonstoichiometric antimony trisulfide pellets prior to the initiation of the present work on silver sulfide.

The Trionics Corporation has investigated the characteristics of nickel oxide as a memory element under the technical direction of Hedden[13]; resistance measurements were made between the two flat surfaces of 20 mil discs. The UNIVAC Research Division made a similar investigation, using nonstoichiometric nickel oxide, prior to the initiation of the present work on silver sulfide. The UNIVAC results are in general agreement with those of Trionics. Beadle[14] evaluated oxide films formed on nickel sheet and obtained much shorter useable life times than were found in the other two investigations of this oxide.

Comparisons of the characteristics of the memory elements, as determined in the UNIVAC studies, are given in Table III-I. The approaches to these studies were slightly different: for example, the switching times for antimony trisulfide were determined with ramp pulses, and thus are to be expected to differ from those determined by square wave pulses for the silver sulfide and nickel oxide. The comparisons shown in the table, consequently, are valid mainly in a general sense; more precise comparisons could be obtained at the expense of repetition of some of the work on the antimony trisulfide and on the nickel oxide.

TABLE III - I

Comparison of the Characteristics of Silver Sulfide, Antimony

Trisulfide, and Nickel Oxide Memory Elements

	SILVER SULFIDE	ANTIMONY TRISULFIDE	NICKEL OXIDE
Preparation			
Fabrication	Silver sulfide with platinum and silver electrodes, pressed into pellets.	Antimony trisulfide with two silver electrodes, pressed into pellets.	Nickel oxide powder pressed into pellets and fired, gold electrodes applied after firing.
Firing	Voltages above 2 V; time of application depends on voltage.	Switches without firing.	Up to 2000 V dc
Operating Characteristics			
Switching Voltage			
High to Low	2 to 12 V	About 300 V dc pulses	About 300 V pulses
Low to High	2 to 12 V	About 15 V dc pulses	About 200 V pulses
Switching Time			
High to Low	15 millisecond pulses without delay	Estimated as less than 100 microseconds, depending on pulse shape.	100 nanosecond pulses, without delay.
Low to High	15 millisecond pulses, without delay.	Pulses of 100 microseconds or less, occurs after termination of the pulse.	Pulses of 30 microseconds or less, occurs after termination of pulse.
Switching Energy			
High to Low	10^{-4} to 1 joule, input energy depending on resistance ratio.	10^{-9} joule, transition energy.	10^{-8} joule, input energy.
Low to High	10^{-4} to 1 joule, input energy depending on resistance ratio.	Not determined	10^{-6} joule, input energy.
Resistances			
High	1000-2000 ohms	10^{8} ohms or more	2×10^{7} to 10^{9} ohms
Low	5 - 10 ohms	200 - 1500 ohms	2000 ohms
Ratio	2×10^{2}	About 10^{5}	10^{4} - 10^{5}

	SILVER SULFIDE	ANTIMONY TRISULFIDE	NICKEL OXIDE
Operating Characteristics _Continued_			
Polarity	Platinum negative for switching high to low	None	None
Reading	2 V peak, 100 kc half wave or single 7 microsecond pulses.	Not determined	1 volt pulses
Life Times	At least 3 x 10⁷ cycles with resist- ance ratios near 10.	Not determined	Not determined
Failure to Switch	About 5%	Not determined	Highly variable; about 1% at best.
Effects of Environment	Information indefinite- ly stable at room temper- ature	Not determined	Information indefi- nitely stable at room temperature.
	Information survives exposure to 125°C and electron irradiation.	Not determined	Not determined
	Operable from -190°C to elevated temperatures at reduced energy.		Operable to 300°C.

Note: As used in this Table, High and low refer to the high resistance state and the
        low resistance state, respectively.

The basic difference among these three compounds is that while silver sulfide is a semiconductor, antimony trisulfide and nickel oxide operate much more like insulators and thus require much higher voltage for switching than does silver sulfide. On the other hand nickel oxide requires much less energy to switch. The high resistance ratio obtained with antimony trisulfide and nickel oxide gives unusually good discrimination between the binary states; nevertheless, the resistance ratio of silver sulfide appears to be adequate. Both antimony trisulfide and nickel oxide switch from the high state to the low state only after delays which were observed to range up to 700 microseconds. No switching path was observed in antimony trisulfide.

On the basis of the present knowledge it would appear that silver sulfide is indeed the preferable choice for a memory element for space applications. However, the acceptance of silver sulfide should not be taken at the exclusion of all other substances. The knowledge so far developed in the area of materials with bistable resistances is extremely meager, and the possibility remains that other substances, or even modification of the presently known substances, might lead to considerably improved materials. Exploratory and foundation researches are clearly needed in this area, and should be undertaken when time permits.